Spring 2016

COMPARISON OF SAMPLE METHODS AND RESULTS FOR HEXAVALENT CHROMIUM EXPOSURES AT LANGLEY AFB

Ericka Crosley
Montana Tech of the University of Montana

COMPARISON OF SAMPLE METHODS AND RESULTS FOR HEXAVALENT CHROMIUM EXPOSURES AT LANGLEY AFB

by

Ericka Crosley

A report submitted in partial fulfillment of the requirements for the degree of

Master of Science

Industrial Hygiene Distance Learning / Professional Track

Montana Tech

2016

Abstract

Various exposure limits and analytical methods are recommended for hexavalent chromium exposures. While the OSHA standard is legally binding, NIOSH and ACGIH recommendations should be considered as well when determining personnel overexposures. Hexavalent chromium is linked to severe acute and chronic effects, including cancer. The United States Air Force currently uses NIOSH methods 7600 and 7605 to sample for hexavalent chromium. This research analyzed if personnel are being overexposed, in addition to comparing NIOSH 7600 and NIOSH 7605 results to determine if both methods are required, or if one can be used in place of both. The results of the sample data analysis indicated that hexavalent chromium samples obtained with both NIOSH methods exceeded the OSHA PEL of 5 ug/m^3In addition, this study revealed that there were no significant differences in hexavalent chromium samples concentrations obtained with both methods.

Keywords: Hexavalent Chromium, NIOSH 7600, NIOSH 7605

Dedication

To my late mother, my father and step-mother, thank you for all of your support. To my daughter Ella – mommy is almost done being busy and we will get to go on a real vacation very soon.

Acknowledgements

Thank you to all the staff at Montana Tech of the University of Montana.

Table of contents

List of Figures

List of Equations

1. Introduction

United States Air Force flightline personnel assigned to the Aerospace Ground Equipment shop at Langley Air Force Base are responsible for maintaining aircraft and missile (weapons systems) structure by removing and re-applying coatings that help protect the weapon systems' metallic and/or composite surface. Maintenance of the coatings is important in order to prevent corrosion and/or deterioration, which can shorten the life-span of the weapons systems, thus endangering personnel and negatively impacting mission accomplishment (IERA, 2000). The coatings used by the Air Force protect the weapons systems from oxidation reactions that degrade the surface and structural support capabilities of the metal or composite material. Since oxygen is present in all environments, it is important for the Air Force to inhibit corrosion of these coatings.

Hexavalent chromium (CrVI) is a corrosion inhibitor, and is present as chromic acid in the pretreatment and as metallic chromate in the primer used for aircraft corrosion control. The most common worker exposures occur during application and/or removal of the pretreatment or primer (IERA, 2000). Application usually occurs via pressurized hoses or hand-held spray guns, during which aerosols are generated that can enter the workers' breathing zone and present an inhalation hazard. Removal, or depainting, is typically performed by mechanical sanding, which can cause release of airborne particulates containing chromates into the worker's breathing zone.

Hexavalent chromium is corrosive to the eyes, skin, and respiratory tract (ICSC, 2016). Repeated or prolonged exposures via inhalation may cause asthma, kidney impairment, and may cause heritable genetic damage to human germ cells; animal tests show that hexavalent chromium may cause toxicity to human reproduction or development (ICSC, 2016). It is a well-established carcinogen associated with lung cancer and nasal and sinus cancer, in addition to non-malignant respiratory effects including irritated, ulcerated, or perforated nasal septa (DHHS, 2013).

There are numerous sampling and analytical methods published for hexavalent chromium, including but not limited to Occupational Safety and Health Administration (OSHA) method ID-215, and National Institute of Occupational Safety and Health (NIOSH) methods 7600 and 7605. The Air Force has strict regulations and does not deviate from current sample methods approved for laboratory analysis.

Currently, both NIOSH methods 7600 and 7605 are used to sample for hexavalent chromium. Alternative sample methods are not currently under consideration by Air Force leadership, so the current NIOSH methods must be used. All hexavalent chromium samples are analyzed at the United States Air Force School of Aerospace Medicine (USAFSAM) Analytical Laboratory located at Wright Patterson Air Force Base, OH (WPAFB), an American Industrial Hygiene Association (AIHA) nationally accredited laboratory.

The (NIOSH) Recommended Exposure Limit (REL) 8-hr Time Weighted Average (TWA) for chromates is 0.0002 mg/m^3 ; while the Occupational Safety and Health Administration (OSHA) Permissible Exposure Limit (PEL) TWA is 0.005 mg/m^3 (NIOSH Pocket Guide, 2015). The OSHA PEL Ceiling is 0.1 mg/m^3 (OSHA, 2016). The ACGIH TLV TWA for chromic acid water-soluble compounds is 0.05 mg/m^3 and 0.01 for water insoluble compounds (OSHA , 2016).

Because of the different recommendations for exposure levels, and the policy for both NIOSH methods to be used, overexposures can be difficult to identify. The Air Force uses OSHA criteria to set their own acceptable levels of exposure. The OSHA Occupational Exposure Limit OEL is used to identify the Action Level (AL), which is 2.5 ug/m^3, or 50% of the OEL. 29 CFR 1910.1026 (f)(1)(ii) requires engineering and work practice controls to reduce and/or maintain employee exposure to hexavalent chromium less than or equal to 2.5 ug/m^3.

This report tested if flightline personnel at Langley Air Force Base are being overexposed to hexavalent chromium and the necessity to sample for both NIOSH methods. Because of the varying exposure limits, it can be difficult to determine if overexposures are occurring.

Hexavalent chromium has serious short and long-term effects due to overexposures, so it is important to ensure personnel are performing painting and de-painting processes without adverse effects. The null hypothesis is that personnel exposures will not exceed 5.0 ug/m^3, which is the OSHA PEL. If overexposures are occurring, additional surveillance requirements may be warranted, along with re-evaluation of control effectiveness. Analyzing sample data from both methods may also provide additional information in determining the requirements for both sampling methods, or using one of the current sampling methods instead of both.

2. Background

2.1. Coating and Primer

Organic coatings (i.e. paint) are carbon-based semi-volatile liquid mixtures of solvents, pigments, reactants, hardeners, dryers, and corrosion inhibitors; the term “coatings” includes chemical surface treatment materials that are not specifically organic in composition, but are required as part of the entire organic coating system (IERA, 2000). The coating system is comprised of a pretreatment (conversion coat), primer, and topcoat. The pretreatment is a chromic/nitric acid mixture that chemically reacts with the metal surface of the weapons systems to form a chromium/aluminum compound that is corrosion resistant and allows for adhesion with the primer (IERA, 2000).

A military specific epoxy primer is used which is yellow in color and is considered a Class C, strontium chromate primer. The primer adds an additional adhesion layer and is comprised of metallic chromate, which inhibits corrosion, and provides resistance to chemicals, lubricants, and corrosive atmospheres. The topcoat is the final finishing layer of the coating system which can add stealth qualities to the weapons system. An activator containing amines is mixed with the binder, and the epoxy and amine functional groups react to form a tough, flexible, corrosion-resistant adhesive.

2.2. Depaint/Paint Process

The inhalation exposure route for hexavalent chromium is the main concern for overexposure occurrences. Personnel performing scuff sanding and/or mechanical abrasion, dust removal, and application of the conversion coat and the primer are monitored for hexavalent chromium exposures via air sampling and routine health exams. Both NIOSH methods 7600 and 7605 are used to sample for hexavalent chromium exposures.

Scuff sanding and mechanical abrasion are performed to remove existing coatings, oxidized paint, and to smooth out nicked, scratched, or chipped paint using mechanical sanders. Ventilated sanders provided some reduction of exposures; however they do not provide complete elimination of dust particles (IERA, 2000). Significant worker exposures to hexavalent chromium occur during scuff sanding and mechanical abrasion (IERA, 2000). During bulk dust removal via compressed air or hand wiping, exposures can occur particularly if the dust is re-suspended in air and into the worker's breathing zone. Application of the conversion coat and primer is performed via paint spray guns, which can also result in inhalation exposures to hexavalent chromium.

Conventional paint spraying is used to apply the primer. The spray gun atomizes the primer using compressed air. Various particle size droplets are generated and propelled from the spray gun onto the surface of the weapons system. Streamlines are formed when particles rebound off the surface of the weapons system. Droplets that do not have sufficient inertia follow the streamlines and do not impact the surface to form a coating; instead, they form a mist or overspray, which can be transported into the workers breathing zone (IERA, 2000).

AFMAN 48-146 (2013) requires chromium levels as low as possible below the OEL. It is not realistic to eliminate CrVI exposures because chromium is present in the coatings used. Respirators are used to reduce personnel exposures to confirmed and/or suspected carcinogens and to maintain an exposure level below the OEL inside the respirator. The assigned protection factor of the respirator is important to identify the actual levels inside the respirator. The APF must be greater than or equal to the exposure divided by the OEL.

Equation 1- APF calculation

$$APF \geq (task\ exposure(ug/m^3)) \div OEL\ ug/m^3 \quad (2)$$

2.3. Toxicology

Hexavalent chromium is reduced to trivalent chromium (chromium III) in the lower respiratory tract by the epithelial lining fluid and by pulmonary alveolar macrophages (Dayan and Paine, 2001). Trivalent chromium is an essential dietary nutrient, whereas hexavalent chromium poses a significant lung cancer risk (CSEM, 2008). Data from animal experiments indicates that with equal solubility, hexavalent chromium compounds penetrate cell membranes and are absorbed more readily than trivalent chromium compounds (CSEM, 2008). Reduction from hexavalent to trivalent chromium occurs inside red blood cells after it is absorbed by erythrocytes. Red blood cell membranes are permeable to hexavalent chromium, but not to trivalent chromium (CSEM, 2008). Excretion of absorbed chromium occurs primarily via urine.

The reduction of hexavalent chromium is considered to serve as a detoxification process when it occurs at a distance from the target sight for toxic or genotoxic effects, while reduction of hexavalent chromium may serve to activate chromium toxicity if it takes place in or near the cell nucleus of target organs (Dayan and Paine, 2001). The rate of reduction and extent of toxicity depends on the balance of hexavalent chromium versus chromium (III).

Hexavalent chromium enters many types of cells and under certain physiological conditions, can be reduced by hydrogen peroxide, glutathione, glutathione reductase, and ascorbic acid to produce reactive intermediates including chromium (IV), chromium (V), thiylradicals, hydroxyl radicals, and ultimately, trivalent chromium (CSEM, 2008). The intermediates produced have been shown to attack DNA, proteins, and membrane lipids, thereby disrupting cellular integrity and functions (De Mattia et al, 2004).

Eventually, the diffusion of hexavalent chromium, the reduction to trivalent chromium and complexing to nucleic acids and proteins within the cell will cause the concentration equilibrium to change (ATSDR, 2000). Once it is absorbed into the bloodstream, trivalent chromium is widely distributed throughout the body into plasma or tissue. The greatest uptake of trivalent chromium as a protein complex is via bone marrow, lungs, lymph nodes, spleen, kidney, and liver; however, autopsy results reveal that chromium levels in the lungs are consistently higher than levels in other organs (ATSDR, 2000).

2.4. Respiratory Effects

When inhaled, chromium compounds are respiratory tract irritants that can result in irritation of the sinuses and airway and lung, nasal, or sinus cancer. Pulmonary irritant effects due to inhalation of chromium include asthma, chronic bronchitis, chronic irritation, chronic pharyngitis, chronic rhinitis, congestion, upper respiratory tract polyps, tracheobronchitis, and ulceration of the nasal mucosa with possible septal perforation (Dayan and Paine, 2001, CSEM 2008). Many cases of nasal mucosa injury (inflamed mucosa, ulcerated septum, and perforated septum) have been reported in workers exposed to hexavalent chromium (ATSDR, 2000). In addition, hexavalent chromium exposures have been associated with symptoms of coughing, wheezing, and dyspnea (CSEM, 2008).

2.5. Cancer

The first epidemiological study of chromate production workers in the United States that demonstrated an association with lung cancer was conducted with 1,445 workers in seven plants engaged in the extraction of chromates from ore in the 1930's and 1940's and resulted in identification of cancer death rates of almost 22%, compared to the expected result of 1.4% (CSEM, 2008). Additional studies found deaths due to lung cancer in chromate production plants from 18% to as high as 60%, with a latency period of approximately 30 years (CSEM, 2008).

Dose-response studies have resulted in a correlation between increased dose and increased exposure time with an increase in the risk of lung cancer. An analysis of lung cancer risk suggests a potential excess risk of death from lung cancer among workers in the United States to exposures above 50 ug/m^3 (Braver et al, 1985). Bena et al (2004) also identified excess risk of lung cancer death resulting from occupational exposure to hexavalent chromium compounds. Stratified analysis of lung cancer mortality showed a trend of increasing mortality with higher cumulative exposure levels, with a latency period of 20-35 years (CSEM, 2008). In addition to lung cancer, a number of epidemiological studies of workers in chromate industries also showed significantly increased risk for nasal and sinus cancers (ATSDR, 2000).

The mechanism of hexavalent chromium carcinogenicity is not completely understood, although the toxicity of chromium within the cell may result from damage to cellular components during the hexavalent chromium to trivalent chromium reduction process by generation of free radicals, including DNA damage (ATSDR, 2000). It may also be possible that non-oxidative mechanisms by be involved in hexavalent chromium carcinogenicity (CSEM, 2008). In addition, the more insoluble the form of hexavalent chromium, the more likely is the risk of cancer due to exposure.

3. Literature Review

. Bioenvironmental Engineers, including IH personnel perform air sampling, send samples to nationally accredited laboratories for testing. The sample results are then documented in DOEHRS (data is electronically transferred from the lab's Laboratory Information Management System (LIMS). The sample results are associated to each personnel's respective record (longitudinal exposure record, or LER), and occupational physicians receive these results for use in medical examinations to determine any possible health effects that may occur due to occupational exposures. In addition, these LER's are used by veterans who may experience latent effects from exposures incurred during their time of service.

It is important to identify the overall chromate exposures by obtaining a cumulative view of both NIOSH chromate methods. In addition, this analysis will allow a comparison of results between the methods, possibly identifying which is more accurate, in addition to identifying worker exposures above the OSHA PEL. A few studies regarding hexavalent chromium exposures in aircraft corrosion control processes have been published and are discussed below.

A study done by Carlton (2003) identified exposures to strontium chromate above the ACGIH TLV-TWA of 0.5 ug/m^3 utilizing NIOSH method 7600. Sampling was performed at Tinker AFB in the Aircraft Corrosion Control shop, with a total of 66 samples collected. The corrosion control processes performed are similar to those at Langley AFB; however the type of aircraft differ slightly – Tinker houses F-16 and C-130 aircraft, while the Langley process was analyzed for personnel working on F-22 aircraft. The mean exposure TWA for the priming process was 83.8 ug/m^3 (Carlton, 2003). The respirators used at Tinker have an APF of 25, which may not be sufficient to prevent exposures above the 0.5 ug/m^3 level, indicating a possible need for a full-face respirator or one with a higher APF. NIOSH method 7605 was not utilized in the study performed by Carlton.

A few studies have been published comparing various NIOSH and OSHA sampling and analysis methods for hexavalent chromium exposures. Boiano et al (2000) performed paired hexavalent chromium air sampling comparing NIOSH method 7600 to OSHA method ID-215 and NIOSH method 7703 (a field-portable method). Twenty field clusters were involved for each of the three methods using PVC sample filters. The sampling techniques are the same for all three methods; however the analysis of the samples differs between all three. OSHA ID-215 uses magnesium sulfate in the extraction, and NIOSH 7703 is a field method using ultrasonic extraction followed by solid-phase extraction in order to isolate the hexavalent chromium (Boiano et al, 2000).

The analysis of variance results for the field samples showed no statistically significant differences among the mean hexavalent chromium concentrations measured by each of the three methods (Boianao et al, 2003). Slightly lower results (statistically significantly lower) were obtained from the OSHA ID-215 method compared to both NIOSH methods 7600 and 7703, possibly due to a loss of hexavalent chromium during the hot plate extraction using magnesium.

Bennet et. al (2015) analyzed hexavalent chromium and isocyanate exposures during the aircraft corrosion control process under crossflow ventilation. Twelve samples were collected and analyzed on personnel working on Hornet strike fighter aircraft on three separate work days. Air samples were collected for various methods for isocyanates and hexavalent chromium. The sampling and analysis method used to measure hexavalent chromium exposures was NIOSH method 7605.

The results for the priming process were above the OSHA PEL in 11 out of the 12 samples, with a mean of 38 ug/m^3 (Bennett et al, 2015). The respirators used have an APF of 50; again raising concerns of exposures above the OSHA PEL inside the respirator. Full-face respirators were recommended based on this study, due to the increased APF of 200 to maximize protection from hexavalent chromium. Variation among some workers was identified; however the variation was contributed to increased work effort.

The research discussed identifies hexavalent chromium exposures above the OSHA PEL; however the key factor in preventing worker exposures is ensuring a respirator with an appropriate APF is utilized. NIOSH method 7605 was not used in the aforementioned studies; thus NIOSH 7600 may be the more common method used. The type of aircraft, depending on size and surface area, may also contribute to a variation in hexavalent chromium exposures across the Air Force in no one specified location. None of the studies found compared NIOSH method 7600 results with NIOSH method 7605 results.

4. Research Design and Methods

In order to compare results and identify if any overexposures are occurring, sample data for both methods will be analyzed for variance to reject or fail to reject the hypotheses. If sample results are statistically similar between methods, it may provide justification for further studies to eliminate one of the methods. The sample data will also be plotted against the OEL for hexavalent chromium in order to test the null hypothesis that exposures are below 5 ug/m^3. Sampling methods, sample data collection, and data analysis are discussed in the following sections, along with limitations of this study.

4.1. Sampling Methods

NIOSH methods 7600 and 7605 are similar in sampling requirements. Both require a 5.0 um polyvinyl chloride (PVC) filter. A 37-mm diameter filter in a polystyrene cassette filter holder is required, with a sampling flow rate between 1-4 L/min. Each method has a different range of analysis; method 7600 identifies hexavalent chromium between 0.05 to 0.2 mg/m^3 and method 7605 identifies hexavalent chromium between 0.05 to 120 ug (0.00005 mg – 0.12 mg)/m^3. Since method 7605 has a lower detection range, and it overlaps method 7600 detection range up to 0.12 mg, it may be possible to eliminate sampling and analyzing for method 7600. Eliminating this method would save man hours in the IH and laboratory shops, and would also save the financial cost of sampling and analyzing for method 7600.

NIOSH method 7600 uses visible ultraviolet radiation (UV-Vis) at 540 nm following a sulfuric acid extraction for sample analysis. Method 7605 also uses ultraviolet radiation at 540 nm; however in this method, the samples are extracted with a sodium hydroxide/sodium carbonate solution. Method 7600 has an estimated limit of detection (LOD) of 0.05 µg, while method 7605 has an estimated LOD of 0.02 µg per sample.

Personal sampling pumps with flexible tubing are connected to the cassette, and the cassette is positioned so the face is parallel to the worker's body. The paired samples were collected from each respective flightline worker. The sampling flow rate was set at 2.0 L/min, within the 1-4 L/min requirement. A sample volume of 200 L was obtained for both methods, with sampling duration of 100 minutes. A Bios DryCal Defender 510 primary calibrator and SKC AirChek® 2000 sampling pump were used for the sampling event, and for all other air sampling performed by IH personnel at Langley AFB. The samples were collected simultaneously to ensure exposure levels were equivalent. The samples were sent to the USAFSAM laboratory within the 14 day holding time (5 days) where they were analyzed. The laboratory then electronically imported the sample results from their Laboratory Information System (LIMS) directly into DOEHRS.

4.2. Data Collection

The Defense Occupational Environmental Health Readiness System (DOEHRS) is a tri-service database (Air Force, Army, and Navy) that is a comprehensive, automated information system for assembling, comparing, evaluating, and storing occupational and environmental health surveillance data, personnel exposure information, workplace environmental monitoring data, personal protective equipment (PPE) usage data, observation of work practices, and employee health hazard educational data. The DOEHRS database provides information needed by Occupational Health staff and command surgeons for reporting options to leadership regarding the reduction of health threats to the services.

IH personnel at Langley AFB perform health risk exposure assessments including sampling, calibration and maintenance, on a daily basis, following AFMAN 48-146 (2013) procedures. The sampling, equipment, and assessment data are then entered into DOEHRS. The data is then reviewed and QA approved by qualified supervisors with the respective QA role in DOEHRS. The sample results are then associated with the personnel's LER. DOEHRS functions so that if calibration and maintenance information are not up-to-date or within specifications, the sample data cannot be QA approved.

Business Objects reporting is a function of DOEHRS that generates reports for various data sets in DOEHRS. A report of air sampling results entered in DOEHRS can be generated for every Air Force location. QA approved air sample data for hexavalent chromium at Langley AFB were generated, and this sample data was entered into IHSTAT for analysis. Fifty samples for method 7600 and 50 samples for method 7605 were used.

4.3. Data Analysis

IHSTAT is a program that provides statistical analysis for health exposure assessment data, including fit tests and exposure data graphs. Each sample data set (7600 and 7605) was entered into IHSTAT to: 1) determine if sample results are below the OSHA PEL, and 2) to compare the sample results from each method to determine any correlation between sample method results. Microsoft Excel was used for comparison of sample results, because IH Stat has a limitation of 50 samples, and does not allow for multiple data sets plotted together. Due to the limitations of IH STAT, Minitab was used to perform analysis of variance using t-tests and analysis of equal variances.

Time Weighted Average (TWA) is calculated in DOEHRS for comparison to the OSHA OEL. TWA is used to estimate exposures over an entire 8-hour work shift.

Equation 2 - 8-hour TWA calculation

$$TWA = exposure\ ((ug/m^3)*(task\ length\ (mins)) \div 480\ min), \qquad (2)$$

where exposure is the concentration, defined below. The task length is the duration of the task time, expressed in minutes.

To determine the actual sample concentration, the sample result is divided by the volume sampled.

Equation 3- Sample Concentration Calculation

$$Concentration\ = sample\ result\ (ug) \div sample\ volume\ (m^3) \tag{3}$$

The sample data will be analyzed using t-tests and analysis of variances in order to test the null hypothesis for personnel exposures stated in the introduction, in addition to the null hypothesis 2: NIOSH method 7600 and 7605 produce results with no significant difference.

The first hypothesis will be tested using a t-test for one sample set for each NIOSH sample method. The second hypothesis will be tested using a test for equal variances and a paired t-test, which uses two sample data sets. Analysis of variance and a line of best fit are also included to determine if the results for both NIOSH methods are statistically significant.

4.4. Limitations

The limitations of this study include the precision and accuracy of the sample methods, any possible sample interferences, and the limited number of samples used. Method 7600 has a precision of 0.084, with an accuracy of +/- 18.58%. Method 7605 has a precision of 0.07 and an accuracy of +/17.4%. Fifty samples were collected for each method, with 100 total samples collected. The greater the number of samples, the greater the confidence can be in any associations made when analyzing the sample data. In addition, minimal research is available comparing the two methods. Several studies in the early 2000's compared NISH 7605 with OSHA method ID-215; however NIOSH methods 7605 and 7600 were not compared.

5. Results

The results from the IHSTAT and Minitab analysis are located in Appendix A. Screenshots of the DOEHRS database and Business Objects reporting can be found in Appendix B. The sample results were used in the TWA calculations to determine the time weighted average of raw sample data results. The sample results are located in Appendix A. Plots of the sample results for both methods are displayed in Figure 1 and Figure 2 below.

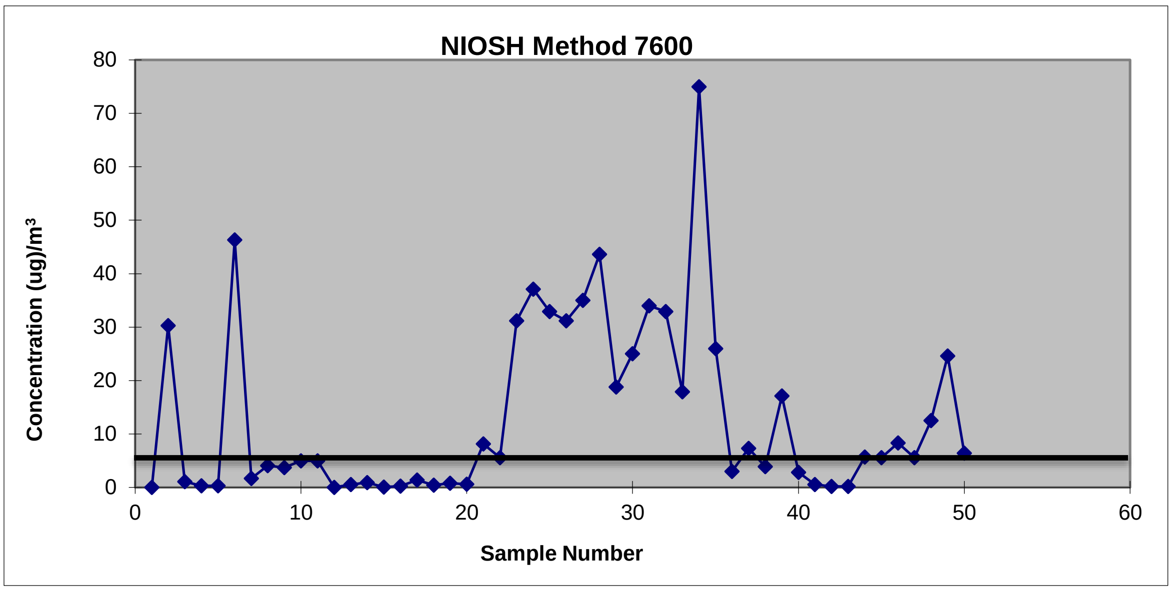


Figure 1 - NIOSH Method 7600 Sample Data 1

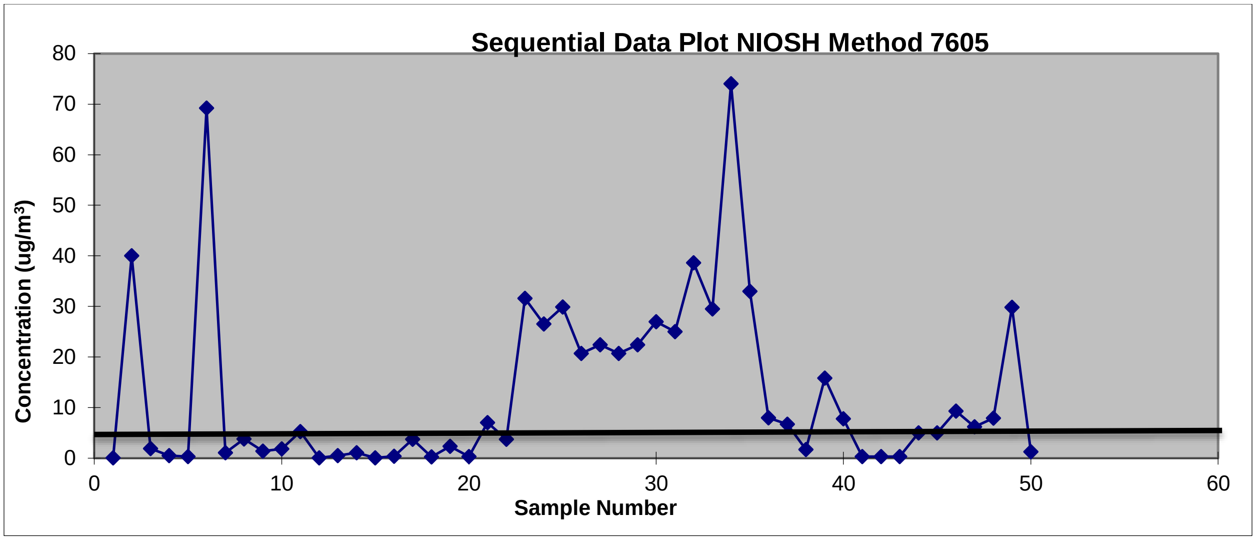


Figure 2 - NIOSH Method 7605 Sample Data 1

Lognormal graphs are generated by taking the natural log of each sample result, and can provide a more normal distribution versus plotting directly the sample data. Lognormal distributions use geometric mean and geometric standard deviation values. For NIOSH method 7600, the correlation coefficient for the lognormal data is 0.914; the closer to 1.0 the correlation coefficient is, the better the fit line. The correlation coefficient for the normal plot is 0.782, so the lognormal plot has the best fit, since the correlation coefficient is closer to 1.

The geometric mean (GM) is the average of the lognormal results, in this case the GM is 3.496, and the geometric standard deviation (GSD) is 9.381. Based on Hewett's rule of thumb, a GSD > 3.5 implies tremendous variability and indicates the process needs further investigation (AIHA, 1998). A 95th percentile value over 100% indicates the need for additional or more effective controls (AIHA, 1998). The % above OEL is 11.734, indicating some overexposures are occurring.

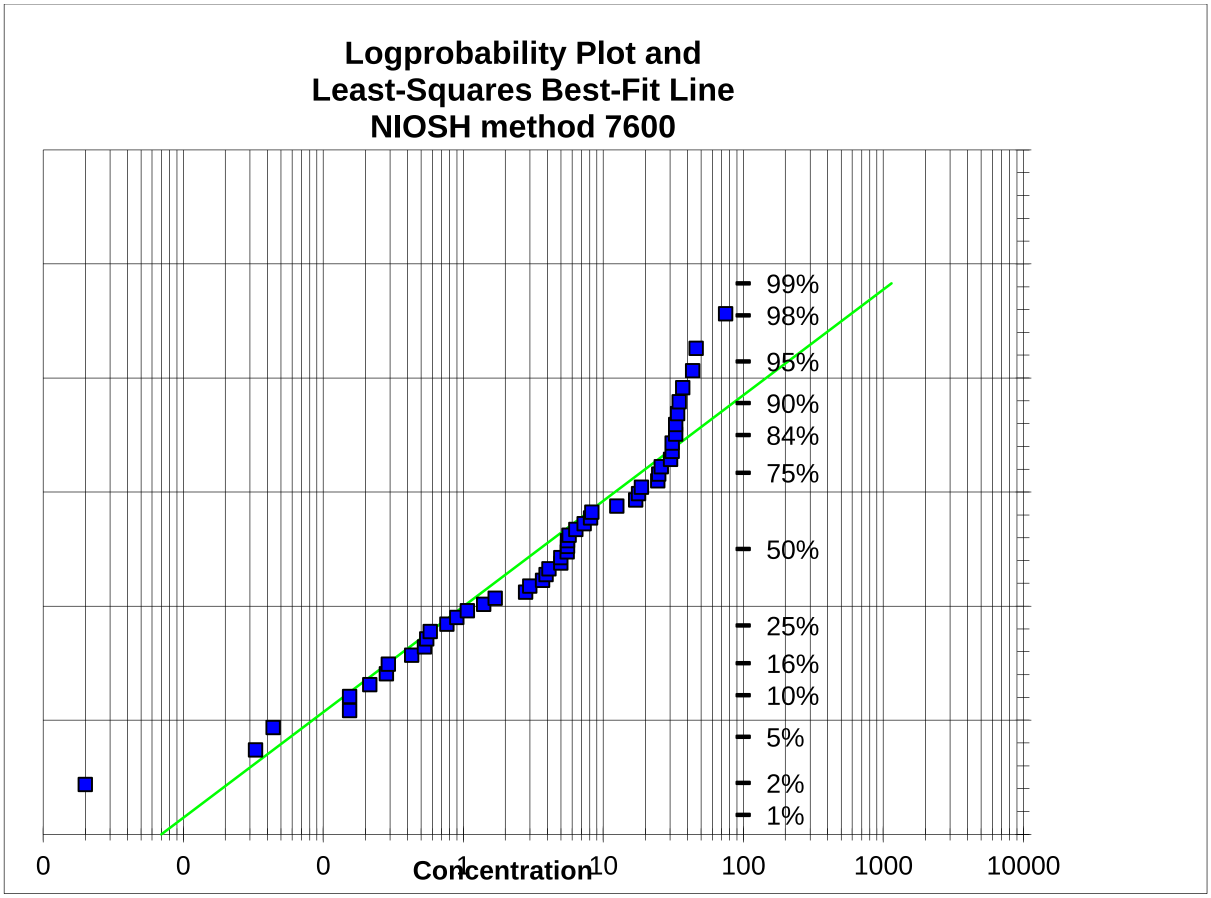


Figure 3 - Lognormal Plot Method 7600 1

NIOSH method 7605 also had a better fit using the lognormal distribution; the correlation coefficient for the lognormal data is 0.926, compared to the coefficient of 0.749 for the normal data set. The GMR is 3.627 and the GSD is 7.709, indicating high variability as did method 7600. Analysis of method 7605 also resulted in a 95th percentile above 100%. The % above OEL is 9.946, again indicating some exposures above the OSHA PEL.

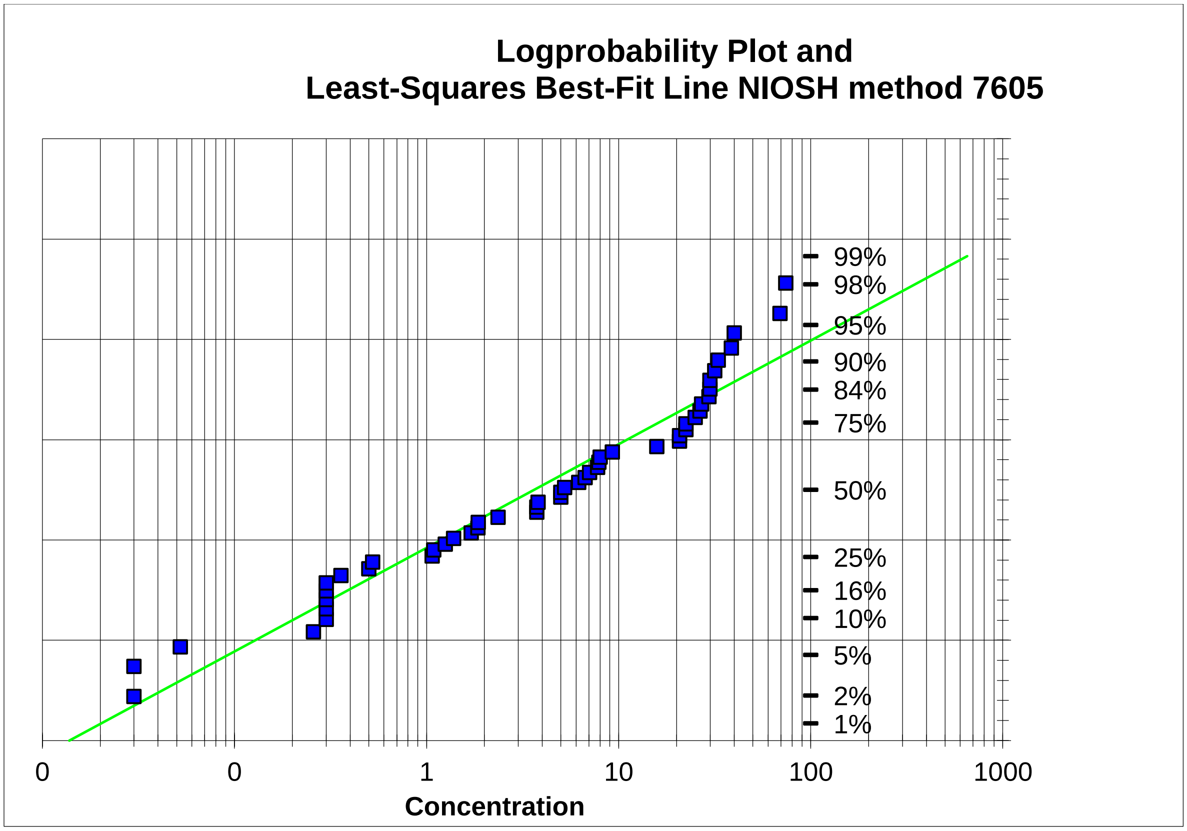


Figure 4 - Lognormal Plot Method 7605 1

Both analyses of the NIOSH methods indicate some exposures above the OSHA PEL may be occurring; however, there is a very high variability as indicated by the GSD. Microsoft Excel was used to plot a comparison graph to compare data points for Methods 7600 and 7605. The plotted results indicate there is some overlap in the methods. Because IH STAT does not allow for multiple data sets, analysis of the comparison of the data sets is limited. Based on the comparison plot, methods 7600 and 7605 do generate comparative sample results.

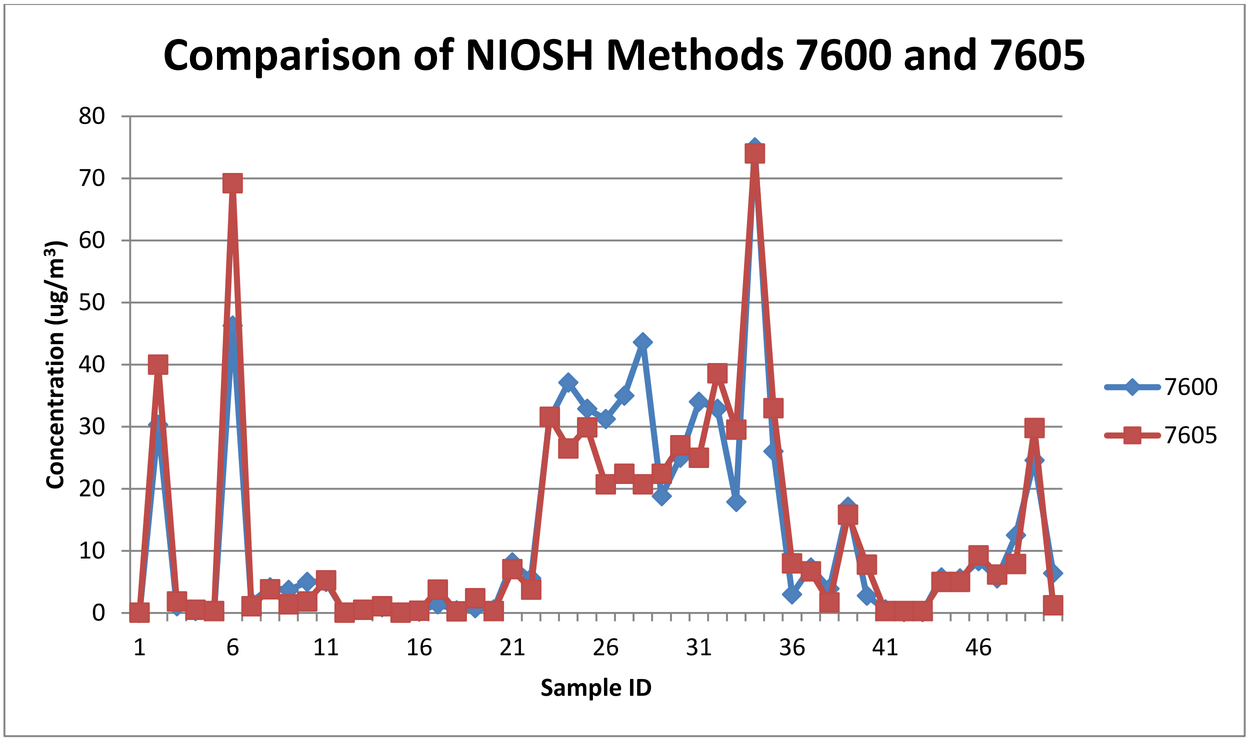


Figure 5 - Comparison of methods 1

Sample data obtained from both the 7600 and 7605 methods were evaluated using IH Stats software as illustrated in Appendix A. These data did not fit a normal distribution or a lognormal distribution. In comparison with the hypothesized mean of 5 ug/m^3, the null hypothesis was that the sample will be less than or equal to 5 ug/m^3. We reject the null for both of sets of analytical methods.

The histograms, shown below, show the sample concentration in ug/m^3 compared to the frequency of each sample concentration. The maximum p-value is 0.001, so the results indicate the null hypothesis should be rejected. If $p< \alpha$, the null hypothesis is rejected. The mean exposures are 13 ug/m^3 using both sample methods, which exceed the OSHA PEL, and the majority of the results, as displayed in the histograms below, are above the OSHA PEL. The 95% lower boundary indicates that 95% of exposures are above 9 ug/m^3, which includes exposures greater than 5 ug/m^3. The null hypothesis will be rejected, indicating exposures are above the OSHA PEL.

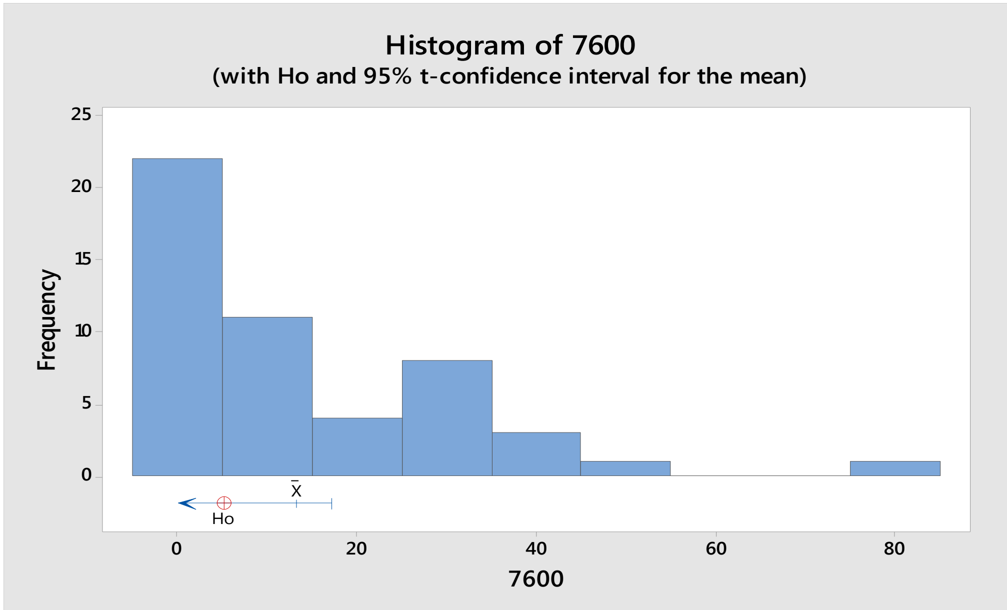


Figure 6 - Method 7600 Histogram 1

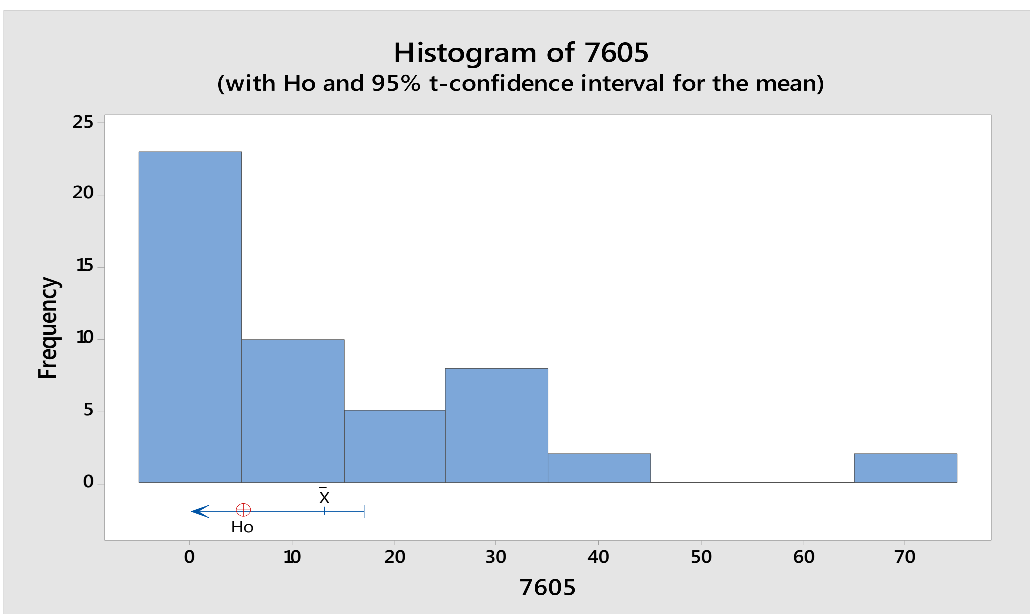


Figure 7 - Method 7605 Histogram 1

The two sample t-test was used to test for null hypothesis 2 for equivalence between sample methods. The results of this test were as follows:

```
Two-sample T for 7600 vs 7605

       N  Mean  StDev  SE Mean
7600  50  13.2   16.4      2.3
7605  50  13.0   17.1      2.4


Difference = μ (7600) - μ (7605)
Estimate for difference:  0.18
95% CI for difference:  (-6.47, 6.84)
T-Test of difference = 0 (vs ≠): T-Value = 0.06  P-Value = 0.956  DF = 97
```

Again, a high p-value and low t-value indicate there is no statistically significant difference between the sample methods. The null hypothesis cannot be rejected. The high standard deviation does indicate a high variance with the results, but not between the methods, since they are within 0.7 between method 7600 and 7605. The result for the Levene's test was also near 1, which confirms the lack of statistical difference between the two methods.

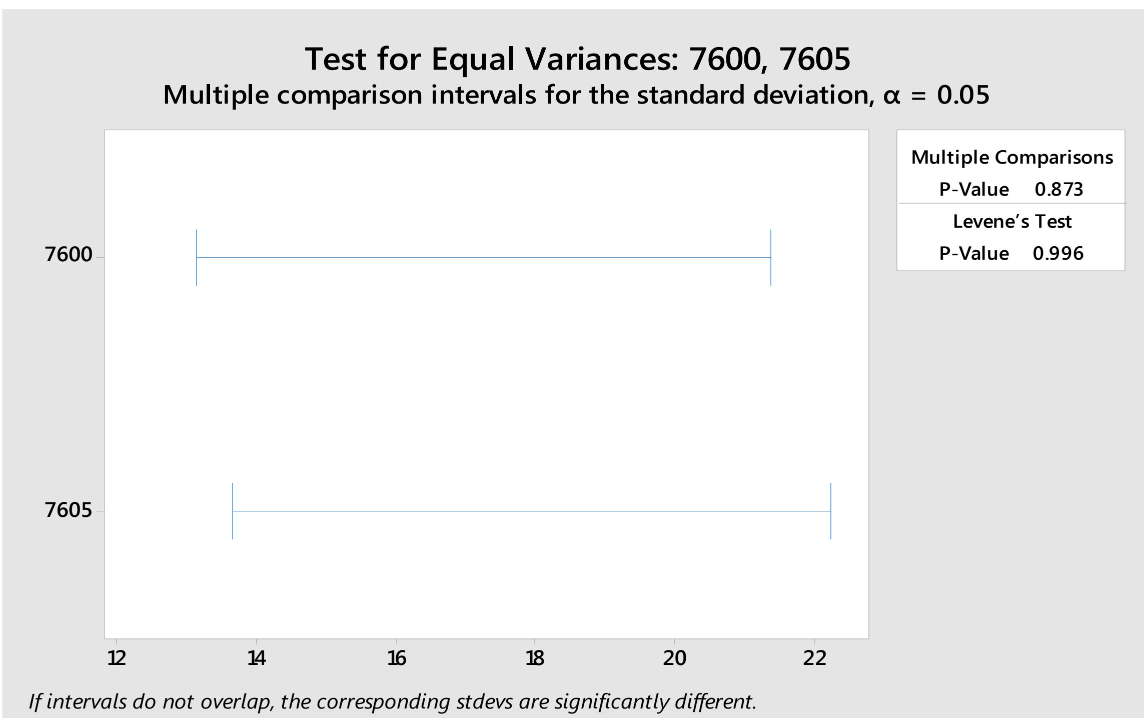


Figure 8 - Test for Equal Variances 1

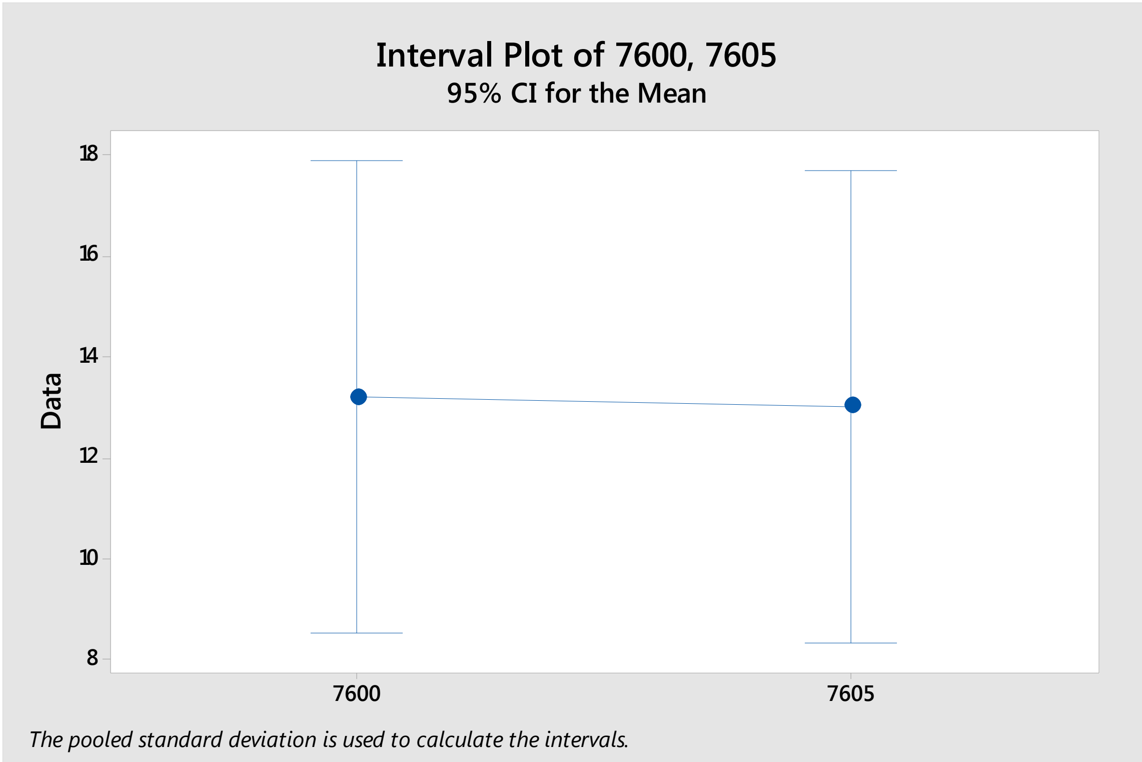


Figure 9 - Confidence Interval Plot 1

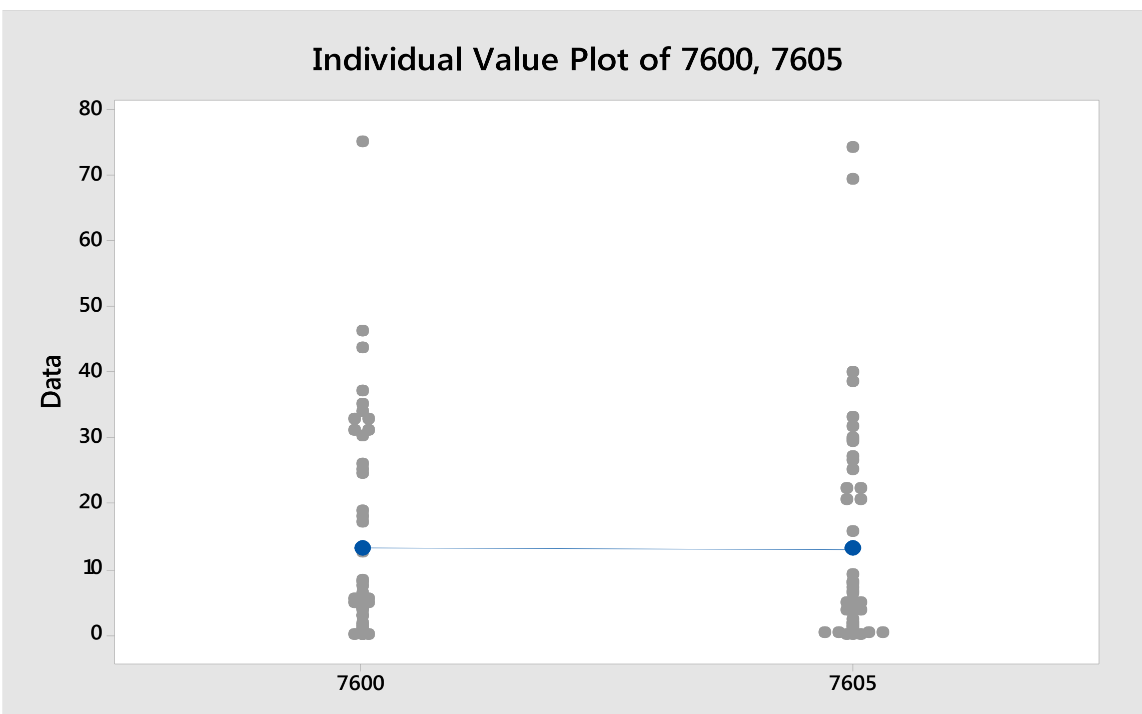


Figure 10 - Minitab Data Point Plot 1

A line of best fit was also generated using Minitab. The paired sample results were analyzed for a line of best fit to compare method 7600 results with method 7605 results. The equation generated was y = 1.594 + 0.8918x, where y = method 7600 results and x = method 7605 results. The correlation coefficient (r^2) for the line of best fit was 0.86. While 0.9 or above is preferred, this is an acceptable correlation coefficient.

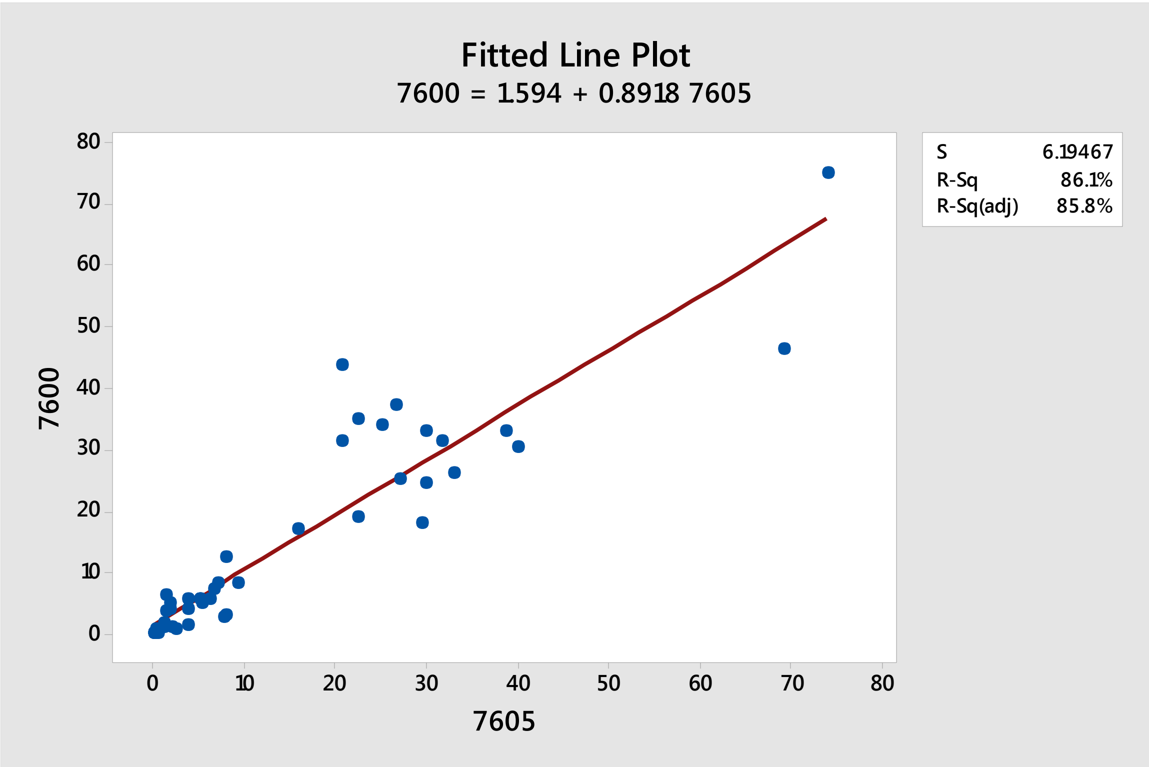


Figure 11. Line of Best Fit 1

6. Discussion, Conclusions, Recommendations for future research

The null hypothesis that exposures are below 5 ug/m^3 was rejected; the IH Stat analysis also indicates there are some exposures above the OSHA PEL and AL. Only with proper respirator use can personnel be confident they are not being overexposed. Without respirator protection, a small percentage of personnel may experience overexposures, which can lead to severe chronic and acute effects. The importance of wearing a respirator properly and accurate fit testing is relevant to the personnel at Langley performing depaint/paint procedures.

The respirators worn by Langley personnel have an APF of 50. The maximum sample results for 7600 and 7605 were 46.3 ug/m^3 and 69.2 ug/m^3, respectively. As mentioned previously, the APF should be greater than the exposure concentration divided by the OEL. Since the OSHA PEL is 5 ug/m^3, the APF of 50 is sufficient to protect workers from overexposures occurring.

The test for equal variance between NIOSH methods does indicate there is no statistical difference between the two methods. Additional analyses need to be performed with larger sample sets in order to confirm the theory that method 7600 and 7605 produce equivalent or similar results. If further research confirms the need for only one sampling and analysis method, eliminating the duplicate method will save time, equipment, supplies, and the financial cost of these as well as reducing laboratory time, equipment, supplies, etc.

It is possible that certain areas of the weapons system depaint/paint process are contaminated more than other areas. For example, if two personnel are priming near each other, the contamination may be higher in that area than if one person was in the area by themselves. This could account for some of the variability within the results.

References Cited

United States Air Force IERA. (June 2000) Aircraft Corrosion Control: Assessment and Reduction of Chromate Exposures. Lt Col Gary Carlton and Maj Ellen England. Brooks AFB, TX.

NIOSH ICSC (International Chemical Safety Cards). (2016) Retrieved 15 January 2016, from: http://www.cdc.gov/niosh/ipcsneng/neng1194.html

NIOSH Pocket Guide(2015). Retrieved on 29 February from: http://www.cdc.gov/niosh/npg/npgd0138.html

OSHA Chemical Sampling Information (2016). Retrieved on 15 January 2016 from: https://www.osha.gov/dts/chemicalsampling/data/CH_228600.html

DHHS (U.S. Department of Health and Human Services), NIOSH, CDC. (September 2013) Occupational Exposure to Hexavalent Chromium. Retrieved from: http://www.cdc.gov/niosh/docs/2013-128/pdfs/2013_128.pdf

United States Dept. of the Air Force. (5 December 2012) Occupational and Environmental Health Program Management (Air Force Manual (AFMAN) 48-146).

Dayan, A., & Paine, A. (2001). Mechanisms of chromium toxicity, carcinogenicity and allergenicity: Review of the literature from 1985 to 2000. *Human & Experimental Toxicology, 20*(9), 439-451.

(CSEM) Agency for Toxic Substances and Disease Registry: Chromium Toxicity. (2008) Case Studies in Environmental Medicine. Retrieved 15 January 2016 from: http://www.atsdr.cdc.gov/csem/chromium/docs/chromium.pdf

Mattia, G. D., Bravi, M. C., Laurenti, O., Luca, O. D., Palmeri, A., Sabatucci, A., . . . Ghiselli, A. (2004). Impairment of cell and plasma redox state in subjects professionally exposed to chromium. *Am. J. Ind. Med. American Journal of Industrial Medicine, 46*(2), 120-125.

ATSDR 2000, Chromium. Retrieved on 15 January 2016 from: http://www.atsdr.cdc.gov/toxprofiles/tp7-c4.pdf

Braver, E. R., Infante, P., & Chu, K. (1985). An analysis of lung cancer risk from exposure to hexavalent chromium. *Journal of Teratogenisis, Carcinogensis, and Mutagenisis, 5*(5), 368-378.

Bennett, J. S., Marlow, D. A., Nourian, F., Breay, J., & Hammond, D. (2016). Hexavalent chromium and isocyanate exposures during military aircraft painting under crossflow ventilation. *Journal of Occupational and Environmental Hygiene, 13*(5), 356-371. Bennett, J. S., Marlow, D. A., Nourian, F., Breay, J., & Hammond, D. (2016).

Carlton, G. N. (2003). Hexavalent Chromium Exposures During Full-Aircraft Corrosion Control. *AIHA J. AIHA Journal, 64*(5), 668.

Boiano, J. M., Wallace, M. E., Sieber, W. K., Groff, J. H., Wang, J., & Ashley, K. (2000). Comparison of three sampling and analytical methods for the determination of airborne hexavalent chromium. *Journal of Environmental Monitoring J. Environ. Monitor., 2*(4), 329-333.

Bennett, J. S., Marlow, D. A., Nourian, F., Breay, J., & Hammond, D. (2016). Hexavalent chromium and isocyanate exposures during military aircraft painting under crossflow ventilation. *Journal of Occupational and Environmental Hygiene*, *13*(5), 356-371.

.

Appendix A: Sample Data and Results

Sample results

Sample	7600	7605
	TWA results ug/m^3	TWA result ug/m^3
1	0.002	0.03
2	30.3	40
3	1.07	1.86
4	0.292	0.5
5	0.283	0.3
6	46.3	69.2
7	1.7	1.09
8	4.1	3.8
9	3.7	1.38
10	5	1.85
11	5	5.23
12	0.033	0.03
13	0.53	0.523
14	0.903	1.07
15	0.044	0.0523
16	0.215	0.358
17	1.4	3.75
18	0.43	0.258
19	0.764	2.36
20	0.582	0.3
21	8.13	7.05
22	5.54	3.75
23	31.2	31.6

24	37.1	26.5
25	32.9	29.9
26	31.2	20.7
27	35	22.4
28	43.6	20.7
29	18.8	22.4
30	25	27
31	34	25
32	32.9	38.6
33	17.9	29.5
34	75	74
35	26	33
36	3	8
37	7.33	6.68
38	3.91	1.71
39	17.1	15.8
40	2.79	7.77
41	0.55	0.3
42	0.155	0.3
43	0.155	0.3
44	5.71	5
45	5.56	5
46	8.33	9.27
47	5.56	6.2
48	12.5	7.9
49	24.6	29.8
50	6.4	1.25

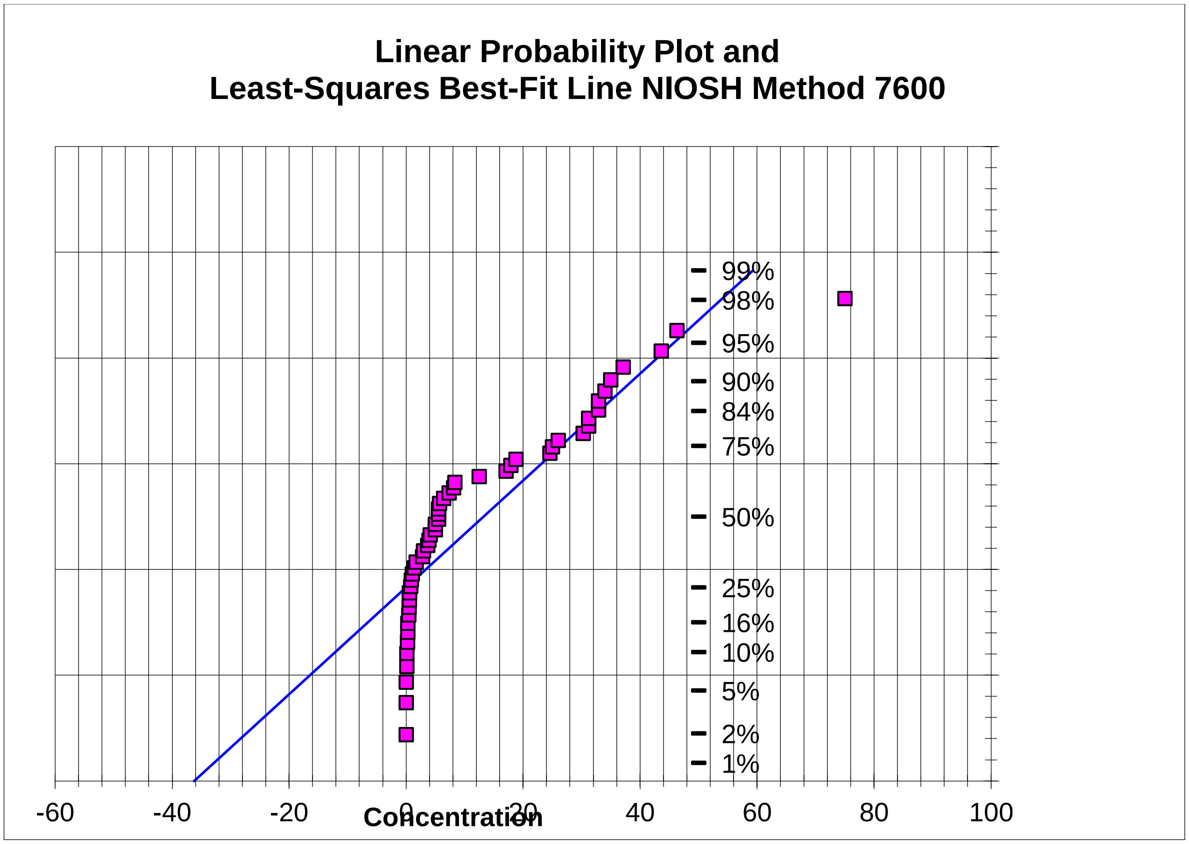
IHSTAT Data

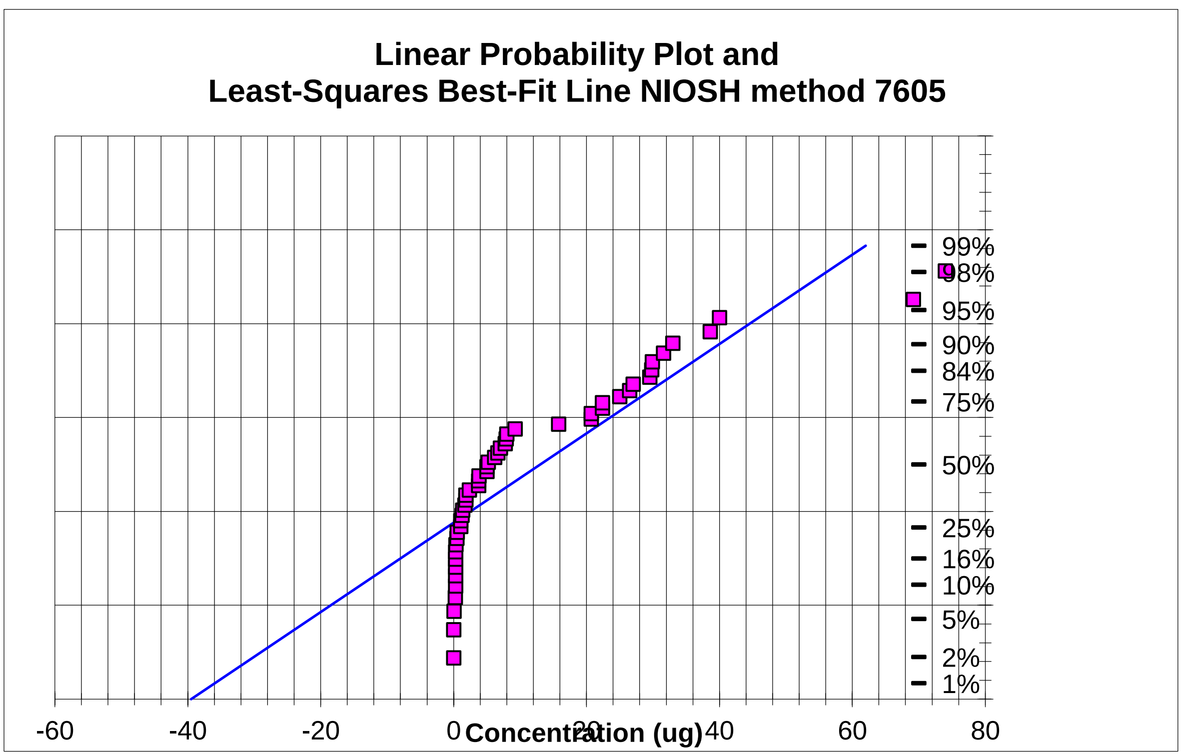
DESCRIPTIVE STATISTICS	
Number of samples (n)	50
Maximum (max)	46.3
Minimum (min)	0.002
Range	46.298
Percent above OEL (%>OEL)	2.000
Mean	13.211
Median	5.550
Standard deviation (s)	16.435
Mean of logtransformed data (LN)	1.252
Std. deviation of logtransformed data (LN	2.239
Geometric mean (GM)	3.496
Geometric standard deviation (GSD)	9.381
TEST FOR DISTRIBUTION FIT	
W-test of logtransformed data (LN)	0.914
Lognormal (a = 0.05)?	No
W-test of data	0.782
Normal (a = 0.05)?	No
LOGNORMAL PARAMETRIC STATISTICS	
Estimated Arithmetic Mean - MVUI	35.835
$LCL_{1,95\%}$ - Land's "Exact"	18.864
$UCL_{1,95\%}$ - Land's "Exact"	145.258
95th Percentile	138.962
$UTL_{95\%,95\%}$	355.829
Percent above OEL (%>OEL)	11.734
$LCL_{1,95\%}$ %>OEL	6.820
$UCL_{1,95\%}$ %>OEL	18.960
NORMAL PARAMETRIC STATISTICS	
Mean	13.211
$LCL_{1,95\%}$ - t statistics	9.315
$UCL_{1,95\%}$ - t statistics	17.108
95th Percentile - Z	40.247
$UTL_{95\%,95\%}$	47.15
Percent above OEL (%>OEL)	1.260

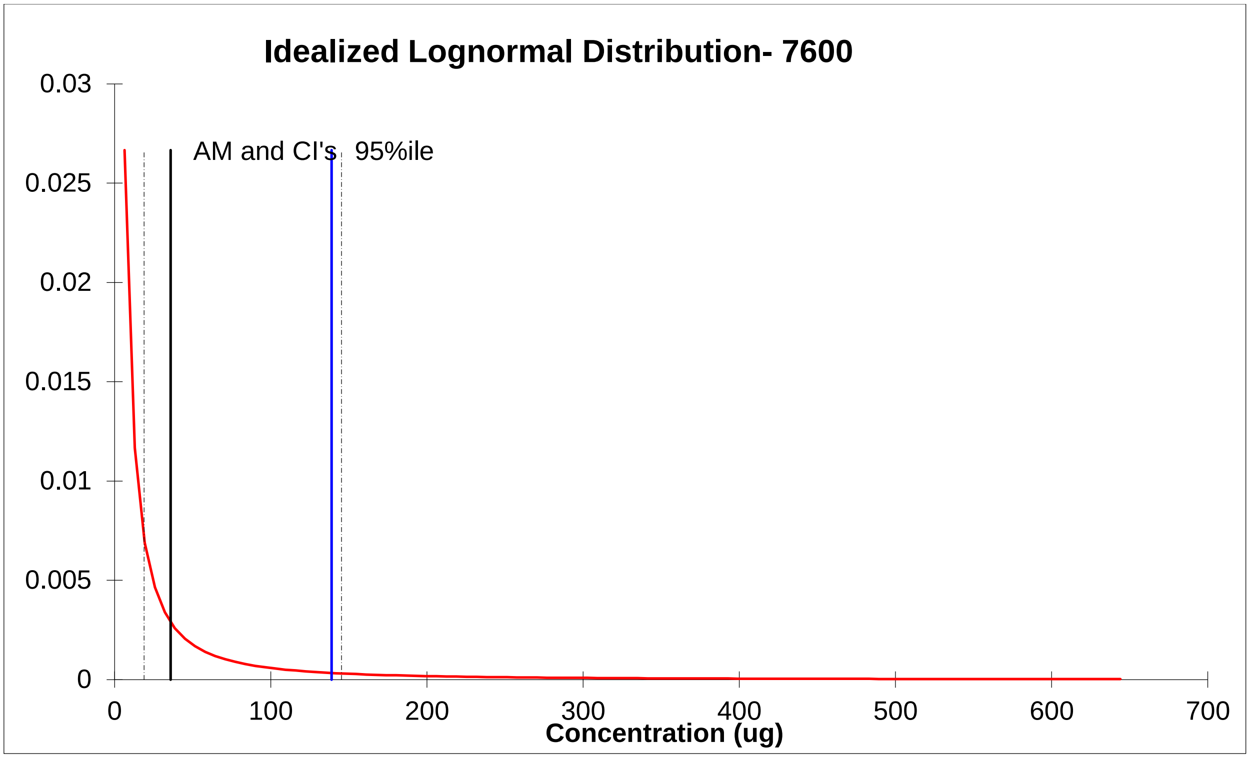
IH STAT RESULTS - NIOSH 7600 1

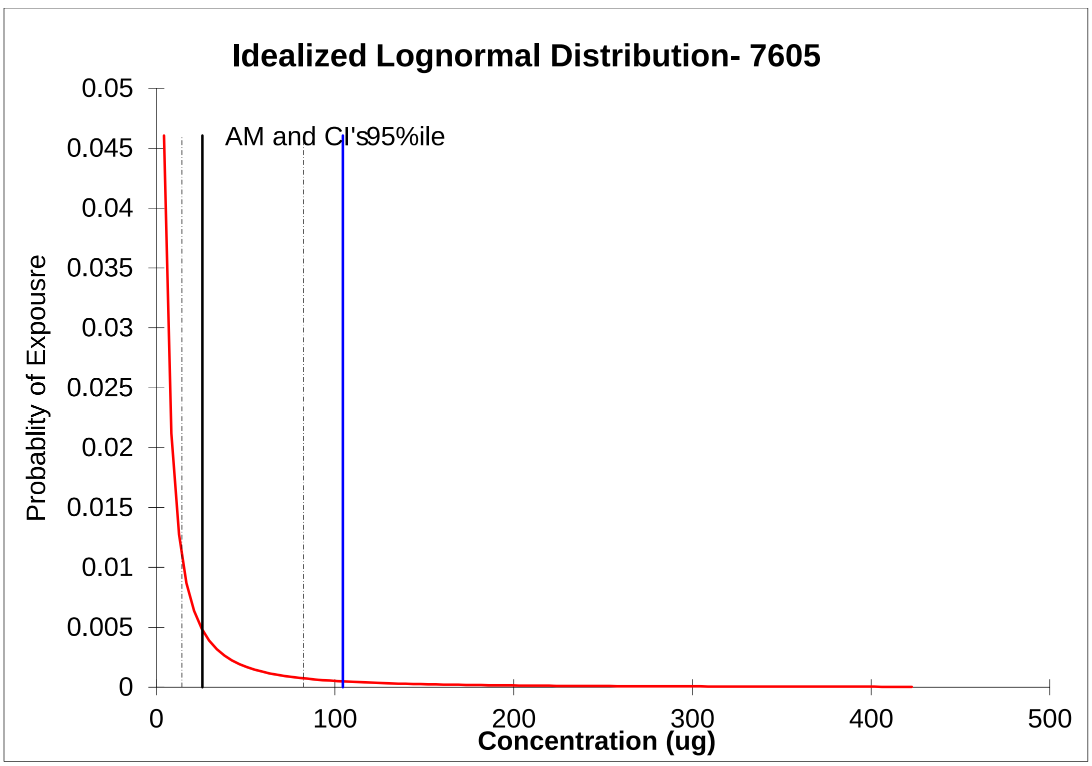
DESCRIPTIVE STATISTICS	
Number of samples (n)	50
Maximum (max)	46.3
Minimum (min)	0.002
Range	46.298
Percent above OEL (%>OEL)	4.000
Mean	13.026
Median	5.115
Standard deviation (s)	17.098
Mean of logtransformed data (LN)	1.288
Std. deviation of logtransformed data (LN	2.042
Geometric mean (GM)	3.627
Geometric standard deviation (GSD)	7.709
TEST FOR DISTRIBUTION FIT	
W-test of logtransformed data (LN)	0.926
Lognormal (a = 0.05)?	No
W-test of data	0.749
Normal (a = 0.05)?	No
LOGNORMAL PARAMETRIC STATISTICS	
Estimated Arithmetic Mean - MVUI	25.721
$LCL_{1,95\%}$ - Land's "Exact"	14.385
$UCL_{1,95\%}$ - Land's "Exact"	82.309
95th Percentile	104.373
$UTL_{95\%,95\%}$	246.105
Percent above OEL (%>OEL)	9.946
$LCL_{1,95\%}$ %>OEL	5.526
$UCL_{1,95\%}$ %>OEL	16.734
NORMAL PARAMETRIC STATISTICS	
Mean	13.026
$LCL_{1,95\%}$ - t statistics	8.973
$UCL_{1,95\%}$ - t statistics	17.080
95th Percentile - Z	41.152
$UTL_{95\%,95\%}$	48.33
Percent above OEL (%>OEL)	1.529

IH STAT RESULTS NIOSH 7605

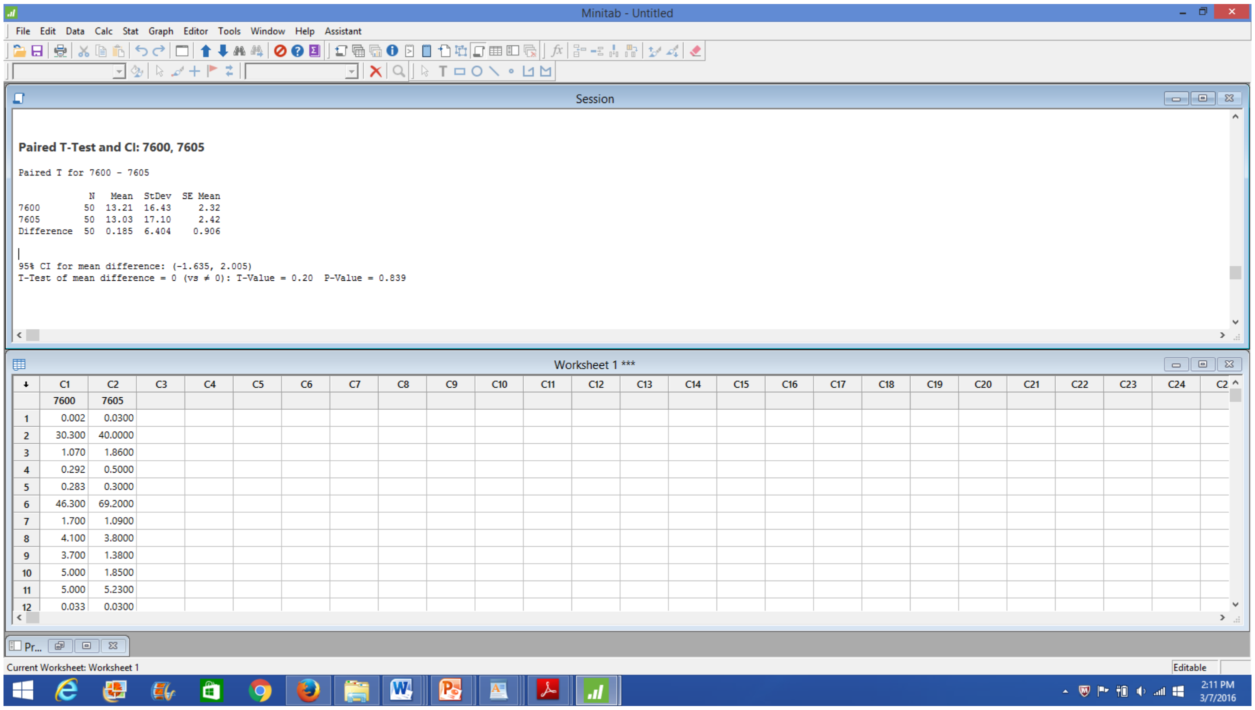

Linear Probability Plot and
Least-Squares Best-Fit Line NIOSH Method 7600
99%
98%
95%
90%
84%
75%
50%
25%
16%
10%
5%
2%
1%
-60
-40
-20
0
20
40
60
80
100
Concentration

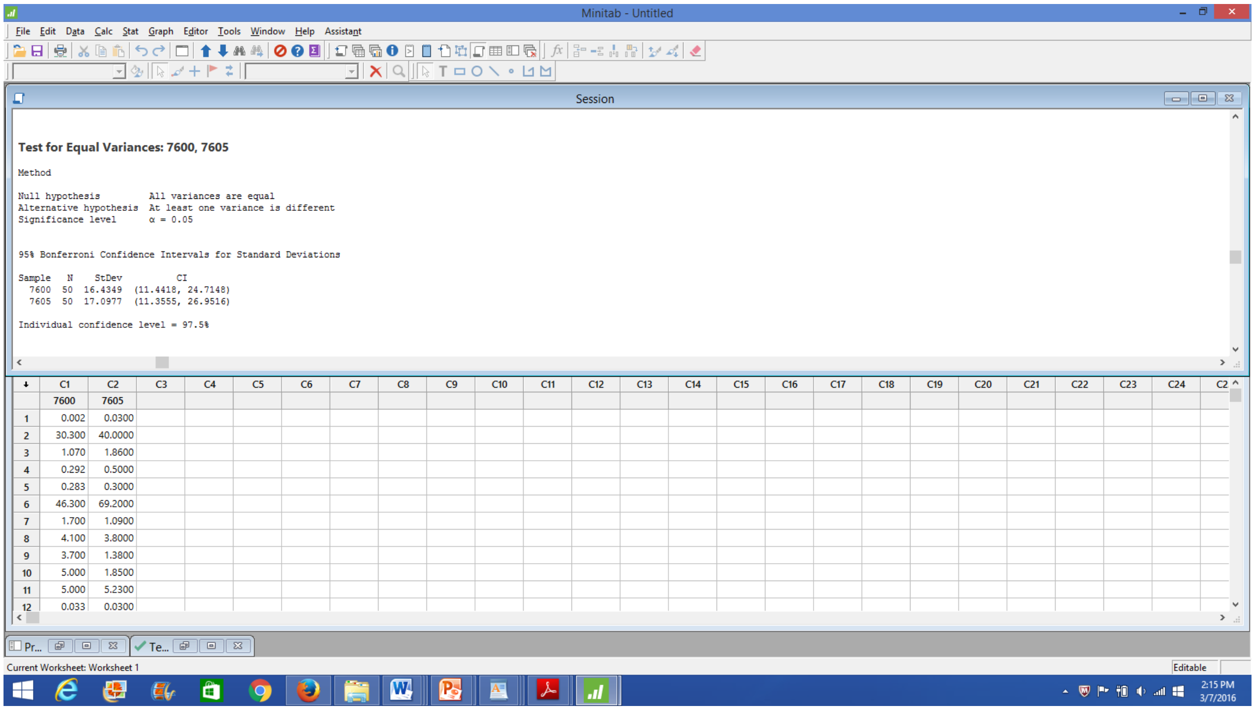

Linear Probability Plot and
Least-Squares Best-Fit Line NIOSH method 7605
99%
98%
95%
90%
84%
75%
50%
25%
16%
10%
5%
2%
1%
-60
-40
-20
0
20
40
60
80
Concentration (ug)

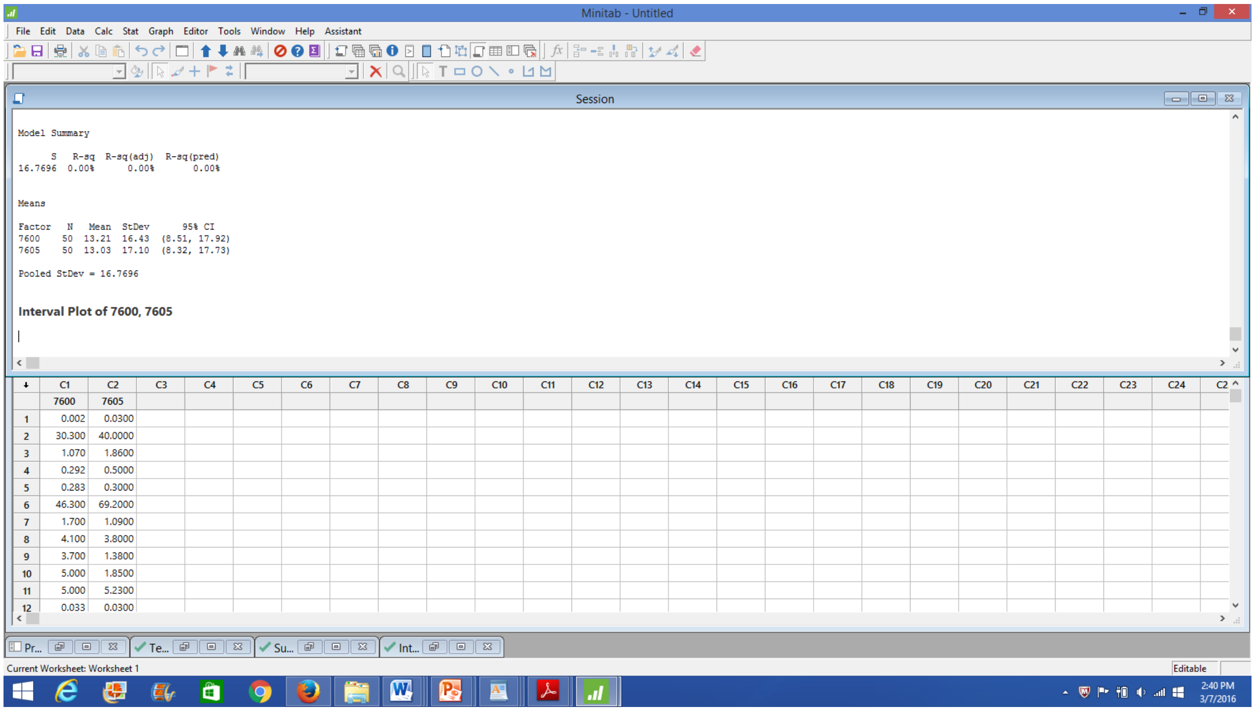

Idealized Lognormal Distribution- 7600
0.03
0.025
0.02
0.015
0.01
0.005
0
AM and CI's
95%ile
0
100
200
300
400
500
600
700
Concentration (ug)


Idealized Lognormal Distribution- 7605
Probablity of Expousre
0.05
0.045
0.04
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
AM and CI's
95%ile
0
100
200
300
400
500
Concentration (ug)

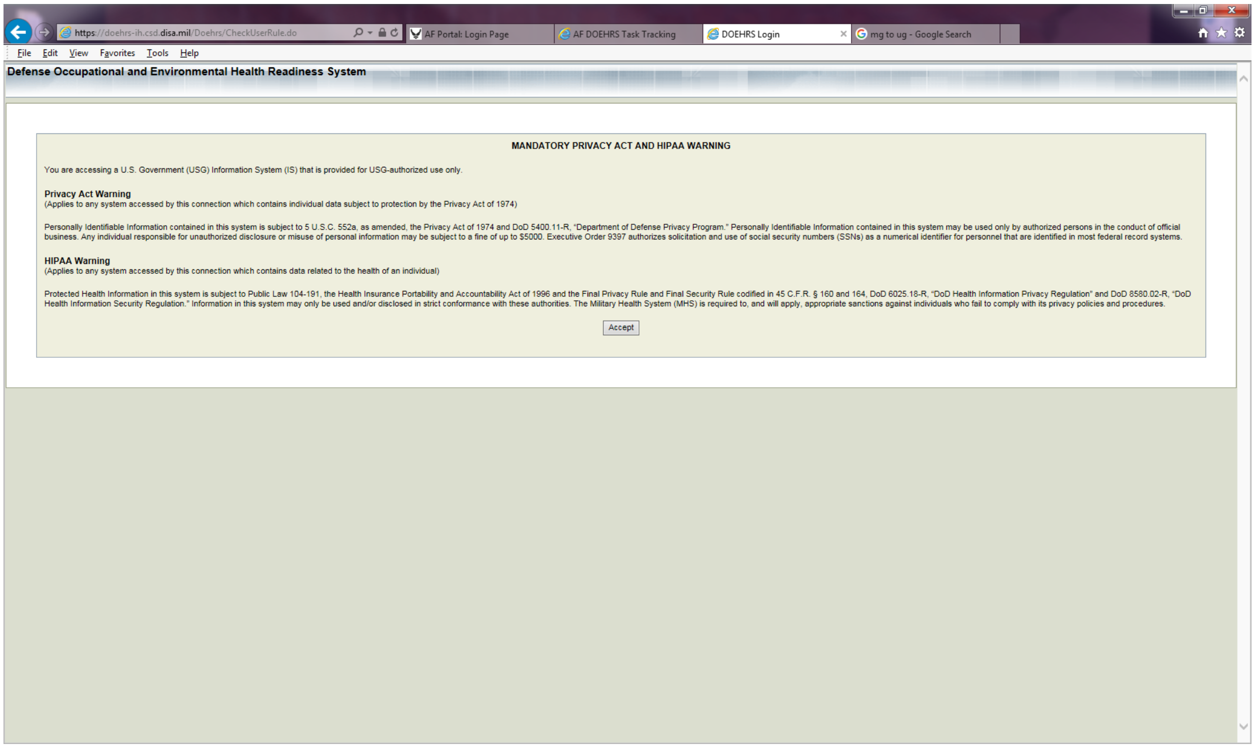
7. Minitab data

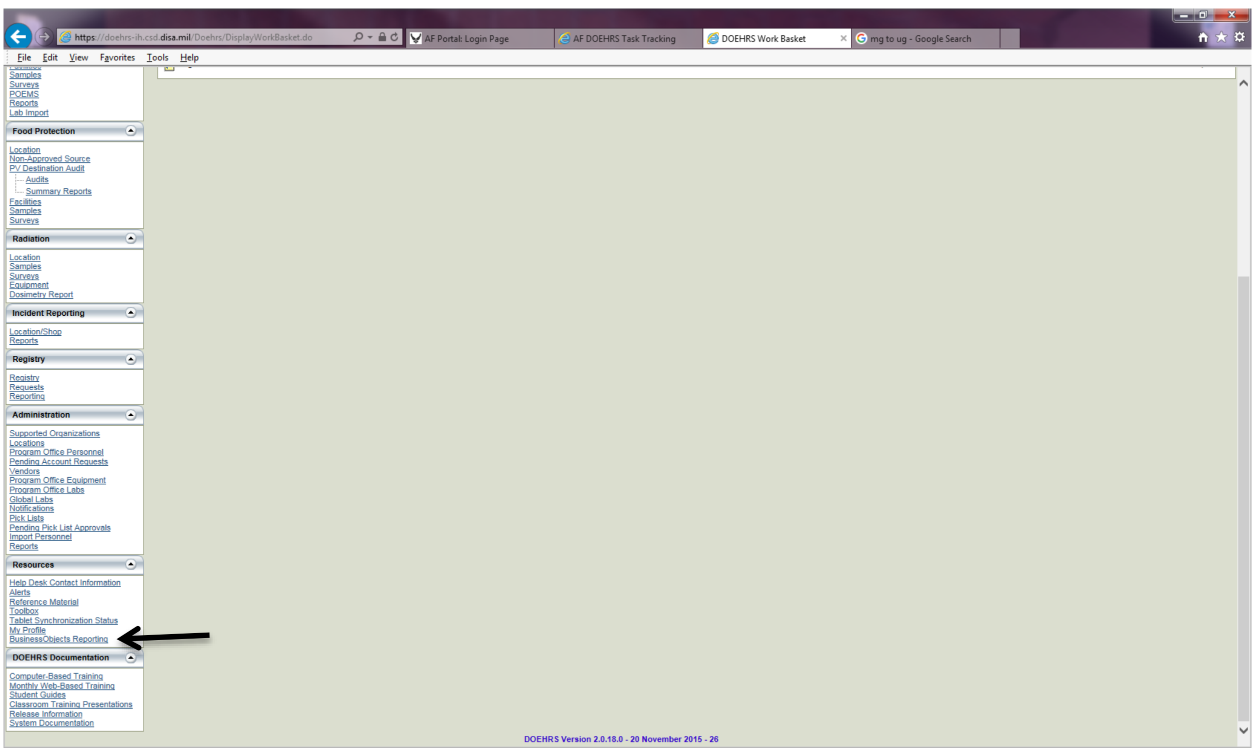


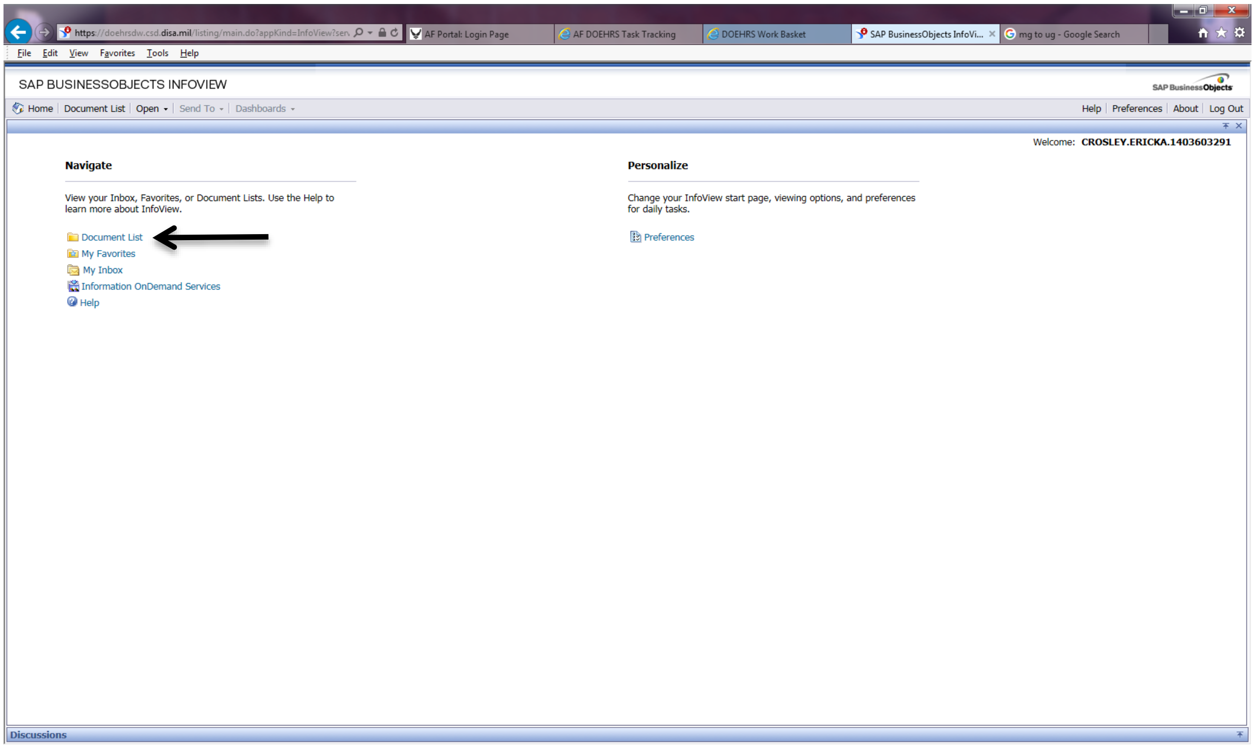



Minitab - Untitled
File Edit Data Calc Stat Graph Editor Tools Window Help Assistant
Session
Model Summary
S R-sq R-sq(adj) R-sq(pred)
16.7696 0.00% 0.00% 0.00%
Means
Factor N Mean StDev 95% CI
7600 50 13.21 16.43 (8.51, 17.92)
7605 50 13.03 17.10 (8.32, 17.73)
Pooled StDev = 16.7696
Interval Plot of 7600, 7605
C1 C2 C3 C4 C5 C6 C7 C8 C9 C10 C11 C12 C13 C14 C15 C16 C17 C18 C19 C20 C21 C22 C23 C24
7600 7605
1 0.002 0.0300
2 30.300 40.0000
3 1.070 1.8600
4 0.292 0.5000
5 0.283 0.3000
6 46.300 69.2000
7 1.700 1.0900
8 4.100 3.8000
9 3.700 1.3800
10 5.000 1.8500
11 5.000 5.2300
12 0.033 0.0300
Pr... Te... Su... Int...
Current Worksheet: Worksheet 1
Editable
2:40 PM
3/7/2016

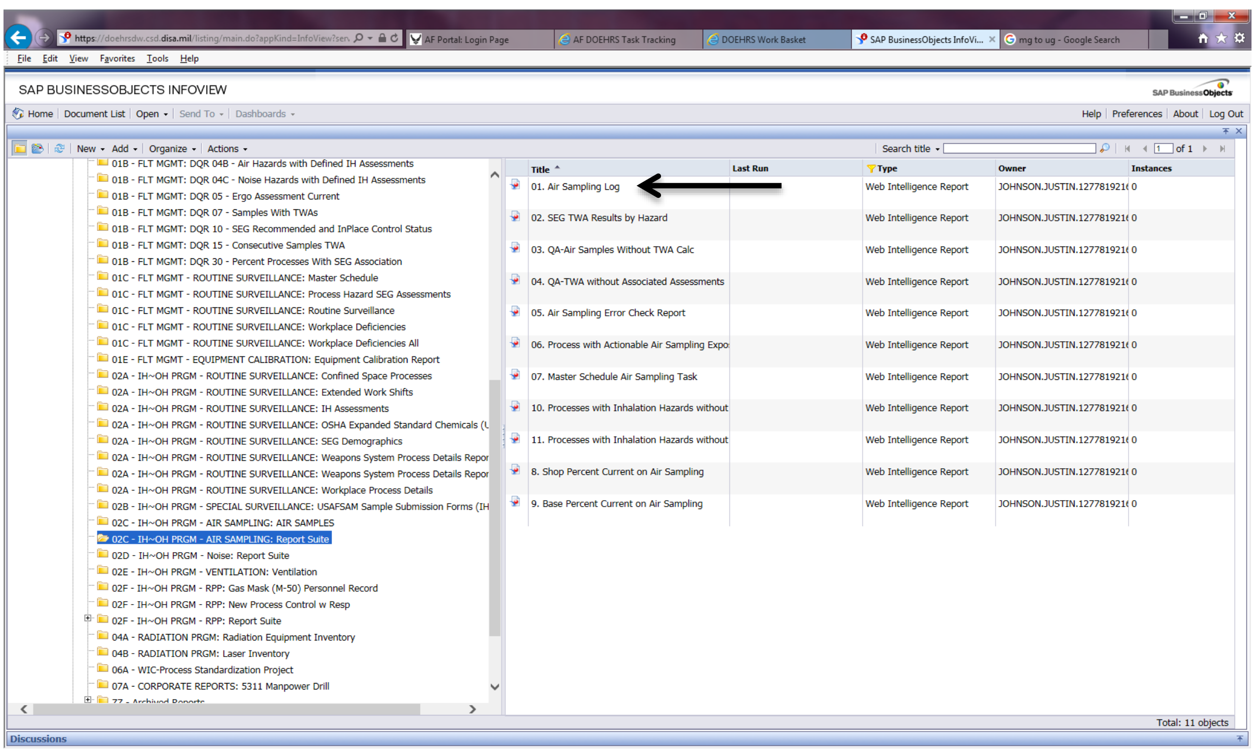
Appendix B: Screenshots of Data pull process



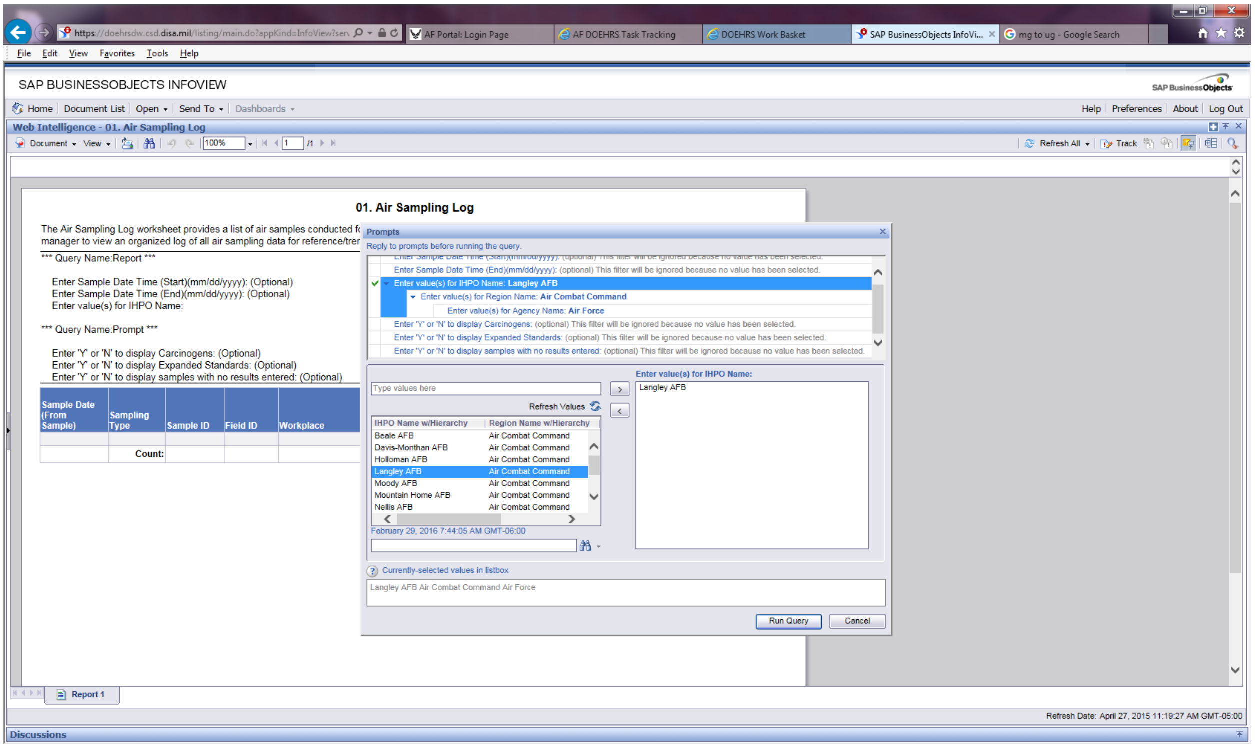


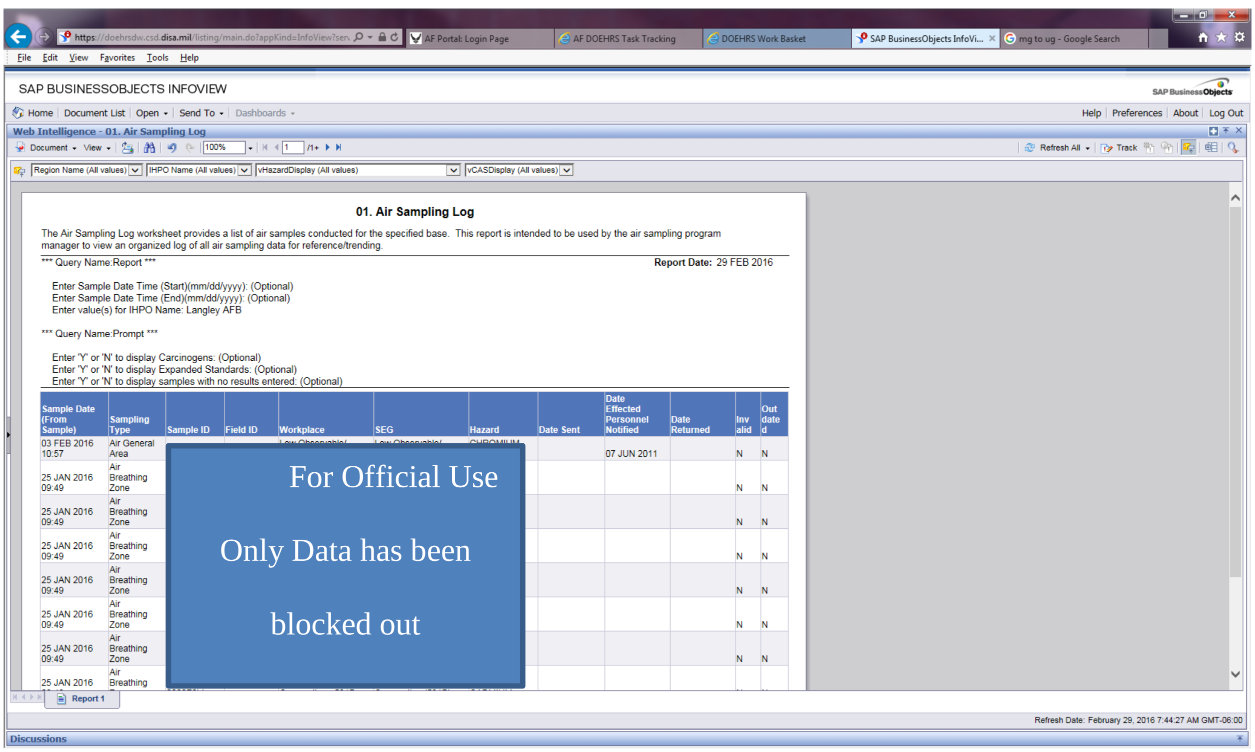


https://doehrsdw.csd.disa.mil/listing/main.do?appKind=InfoView&service=
AF Portal: Login Page
AF DOEHRS Task Tracking
DOEHRS Work Basket
SAP BusinessObjects InfoVi...
mg to ug - Google Search
File Edit View Favorites Tools Help
SAP BUSINESSOBJECTS INFOVIEW
SAP BusinessObjects
Home Document List Open Send To Dashboards
Help Preferences About Log Out
Welcome: CROSLEY.ERICKA.1403603291
Navigate
View your Inbox, Favorites, or Document Lists. Use the Help to learn more about InfoView.
Document List
My Favorites
My Inbox
Information OnDemand Services
Help
Personalize
Change your InfoView start page, viewing options, and preferences for daily tasks.
Preferences
Discussions



https://doehrsdw.csd.disa.mil/listing/main.do?appKind=InfoView&service=
AF Portal: Login Page
AF DOEHRS Task Tracking
DOEHRS Work Basket
SAP BusinessObjects InfoVi...
mg to ug - Google Search
File Edit View Favorites Tools Help
SAP BUSINESSOBJECTS INFOVIEW
SAP BusinessObjects
Home Document List Open Send To Dashboards
Help Preferences About Log Out
New Add Organize Actions
Search title
1 of 1
01B - FLT MGMT: DQR 04B - Air Hazards with Defined IH Assessments
01B - FLT MGMT: DQR 04C - Noise Hazards with Defined IH Assessments
01B - FLT MGMT: DQR 05 - Ergo Assessment Current
01B - FLT MGMT: DQR 07 - Samples With TWAs
01B - FLT MGMT: DQR 10 - SEG Recommended and InPlace Control Status
01B - FLT MGMT: DQR 15 - Consecutive Samples TWA
01B - FLT MGMT: DQR 30 - Percent Processes With SEG Association
01C - FLT MGMT - ROUTINE SURVEILLANCE: Master Schedule
01C - FLT MGMT - ROUTINE SURVEILLANCE: Process Hazard SEG Assessments
01C - FLT MGMT - ROUTINE SURVEILLANCE: Routine Surveillance
01C - FLT MGMT - ROUTINE SURVEILLANCE: Workplace Deficiencies
01C - FLT MGMT - ROUTINE SURVEILLANCE: Workplace Deficiencies All
01E - FLT MGMT - EQUIPMENT CALIBRATION: Equipment Calibration Report
02A - IH~OH PRGM - ROUTINE SURVEILLANCE: Confined Space Processes
02A - IH~OH PRGM - ROUTINE SURVEILLANCE: Extended Work Shifts
02A - IH~OH PRGM - ROUTINE SURVEILLANCE: IH Assessments
02A - IH~OH PRGM - ROUTINE SURVEILLANCE: OSHA Expanded Standard Chemicals (U
02A - IH~OH PRGM - ROUTINE SURVEILLANCE: SEG Demographics
02A - IH~OH PRGM - ROUTINE SURVEILLANCE: Weapons System Process Details Repor
02A - IH~OH PRGM - ROUTINE SURVEILLANCE: Weapons System Process Details Repor
02A - IH~OH PRGM - ROUTINE SURVEILLANCE: Workplace Process Details
02B - IH~OH PRGM - SPECIAL SURVEILLANCE: USAFSAM Sample Submission Forms (IH
02C - IH~OH PRGM - AIR SAMPLING: AIR SAMPLES
02C - IH~OH PRGM - AIR SAMPLING: Report Suite
02D - IH~OH PRGM - Noise: Report Suite
02E - IH~OH PRGM - VENTILATION: Ventilation
02F - IH~OH PRGM - RPP: Gas Mask (M-50) Personnel Record
02F - IH~OH PRGM - RPP: New Process Control w Resp
02F - IH~OH PRGM - RPP: Report Suite
04A - RADIATION PRGM: Radiation Equipment Inventory
04B - RADIATION PRGM: Laser Inventory
06A - WIC-Process Standardization Project
07A - CORPORATE REPORTS: 5311 Manpower Drill
Title
Last Run
Type
Owner
Instances
01. Air Sampling Log
02. SEG TWA Results by Hazard
03. QA-Air Samples Without TWA Calc
04. QA-TWA without Associated Assessments
05. Air Sampling Error Check Report
06. Process with Actionable Air Sampling Expo
07. Master Schedule Air Sampling Task
10. Processes with Inhalation Hazards without
11. Processes with Inhalation Hazards without
8. Shop Percent Current on Air Sampling
9. Base Percent Current on Air Sampling
Web Intelligence Report
JOHNSON.JUSTIN.127781921
0
Total: 11 objects
Discussions


SAP BUSINESSOBJECTS INFOVIEW
Web Intelligence - 01. Air Sampling Log
01. Air Sampling Log
The Air Sampling Log worksheet provides a list of air samples conducted f
manager to view an organized log of all air sampling data for reference/tren
*** Query Name:Report ***
Enter Sample Date Time (Start)(mm/dd/yyyy): (Optional)
Enter Sample Date Time (End)(mm/dd/yyyy): (Optional)
Enter value(s) for IHPO Name:
*** Query Name:Prompt ***
Enter 'Y' or 'N' to display Carcinogens: (Optional)
Enter 'Y' or 'N' to display Expanded Standards: (Optional)
Enter 'Y' or 'N' to display samples with no results entered: (Optional)
Sample Date (From Sample)
Sampling Type
Sample ID
Field ID
Workplace
Count:
Prompts
Reply to prompts before running the query.
Enter value(s) for IHPO Name: Langley AFB
Enter value(s) for Region Name: Air Combat Command
Enter value(s) for Agency Name: Air Force
Enter value(s) for IHPO Name:
Langley AFB
Beale AFB
Davis-Monthan AFB
Holloman AFB
Langley AFB
Moody AFB
Mountain Home AFB
Nellis AFB
Currently-selected values in listbox
Langley AFB Air Combat Command Air Force
Run Query
Cancel
Report 1
Refresh Date: April 27, 2015 11:19:27 AM GMT-05:00
Discussions


SAP BUSINESSOBJECTS INFOVIEW
Web Intelligence - 01. Air Sampling Log
01. Air Sampling Log
The Air Sampling Log worksheet provides a list of air samples conducted for the specified base. This report is intended to be used by the air sampling program
manager to view an organized log of all air sampling data for reference/trending.
*** Query Name:Report ***
Report Date: 29 FEB 2016
Enter Sample Date Time (Start)(mm/dd/yyyy): (Optional)
Enter Sample Date Time (End)(mm/dd/yyyy): (Optional)
Enter value(s) for IHPO Name: Langley AFB
*** Query Name:Prompt ***
Enter 'Y' or 'N' to display Carcinogens: (Optional)
Enter 'Y' or 'N' to display Expanded Standards: (Optional)
Enter 'Y' or 'N' to display samples with no results entered: (Optional)
Sample Date (From Sample)
Sampling Type
Sample ID
Field ID
Workplace
SEG
Hazard
Date Sent
Date Effected Personnel Notified
Date Returned
Inv alid
Out date d
03 FEB 2016 10:57
Air General Area
07 JUN 2011
25 JAN 2016 09:49
Air Breathing Zone
For Official Use
Only Data has been
blocked out
Report 1
Refresh Date: February 29, 2016 7:44:27 AM GMT-06:00
Discussions